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ANNUAL AFOSR CHEMISTRY PROGRAM REVIEW (19th)

Denton W. Elliott

Air Force Office of Scientific Research
Arlington, Virginia

January 1974

COVER

The diagram on the cover depicts the ligand-bridged structure of mixed valence palladium and platinum complexes of the type $M(A)_nX_3$, when M = Pd or Pt; A = NH_3, $C_2H_5NH_2$, or ethylenediamine; and X = Cl, Br, or I. The conductivities of these complexes at high pressures are being investigated by Drs. Interrante and Kasper of General Electric under a contract with the Directorate of Chemical Sciences of AFOSR. This study, along with inputs from theoretical calculations, has led to a better fundamental understanding of the mechanism for electronic conduction in such materials together with detailed information relating conductivity and molecular structure.

ABSTRACT

This review provides a record of research in progress, along with illustrative achievements resulting from the basic research program of the Directorate of Chemical Sciences, Air Force Office of Scientific Research (AFSC). The first section of the three principal sections presents various technical aspects. It contains articles on the JANAF Thermochemical Tables, AFOSR Organometallic Chemistry Research Program, Past and Present, Electrochemistry, and Surface Chemistry. The second section contains program statistics. The third section consists of research efforts completed in Fiscal Year 1973.

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FY 73

DENTON W. ELLIOTT, Editor

MAJ DAVID S. OLSON, Managing Editor

January 1974

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH (AFSC)
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The Directorate obtains and maintains for the Air Force a diversified program of chemical research through support of scientists in promising original endeavors of their own choosing. The Directorate also functions as a dynamic interface between the Air Force and the scientific community, ensuring the free, full, and constant interchange of ideas from each to the other through publications, personal contacts, meeting attendance, and sponsored symposia. In these ways the Directorate aids the Air Force in its maintenance of technological superiority.

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1 January 1974

TO: Members of the Chemistry Research Evaluation Panel

The period covered by this review is 1 July 1972 to 30 June 1973. We are, in other words, a bit late. The period was, however, an extraordinarily active one in the Directorate of Chemical Sciences as well as AFOSR as a whole.

Just prior to the inception of the fiscal year 1972 Amos Horney retired after more than twenty years as Director of Chemical Sciences. During the year three people served as Acting Director: first, Denton Elliott; next, Colonel Jack Comerford; and, finally, myself.

Important changes at AFOSR included formal elimination of the Division structure that existed in some Directorates. Affected was the Energetics Division of the Directorate of Aeromechanics. Additionally, a chemically oriented project, Kinetics and Thermophysical Properties, was transferred to the Directorate of Chemical Sciences along with two program managers - Dr. J. F. Masi and (then) Captain David Olson.

We joined with the new personnel to reorganize the Directorate Program into seven tasks (or categories) of chemistry and energy conversion: chemical techniques, chemical structures, surface chemistry, molecular dynamics, chemical reactivity and properties, kinetics of energetic species, and thermophysical properties. Together with changes in people and changes in program there was an even more important source of program impact - change in budget. Between FY 72 and FY 73 the resources available for the joint chemistry program dropped by almost 23%!

We are proud of what we accomplished in FY 73, the record of which is contained in the pages to follow. We have strived to increase the quality of the science and maximize the impact on Air Force technology while resources dwindled. I believe we did so successfully.

Cordially yours,

Donald L. Ball

DONALD L. BALL
Director of Chemical Sciences

A Status Report From Abroad

(This article was written by Major D. E. Dodds, Head of Physical and Environmental Sciences, European Office of Aerospace Research. Professor E. W. Schlag was formerly at Northwestern University. His research has been supported by the Chemistry Directorate, both while he was at Northwestern and at Munich.)

At the Institute for Physical Chemistry in Munich, Prof. E. W. Schlag's work encompasses three areas: determination of excited state lifetimes, photoionization resonance and development of tunable dye lasers as excitation sources.

Excited State Lifetimes - Schlag's effort to measure the lifetimes of the first excited singlet state of large molecules (e.g., anthracene and naphthalene) began at Northwestern University and continued during and after his move to Munich in 1971. Equipment brought from the US arrived in March 1972. He has three people in the laboratory determining excited state lifetimes: Howard, Selzle, and Schroeder. Howard came with him from Northwestern. In about six months they expect to be getting an apparatus to measure quantum yields. Coupled with lifetime measurements, this will give them the capability to investigate intersystem crossing mechanisms and efficiencies.

Photoionization Resonance - Schlag's group developing a photoionization resonance (PIR) technique is ably headed by Herbert Pollak who is assisted by B. Gotchev and O. Kalman. Fundamentally, the PIR technique measures the quantity of electrons generated having zero kinetic energy (resonance electrons) versus the energy of the ionizing radiation. Crossed beam of about 10^{10} photons/sec and 10^{9} molecules/sec are expected to result in about 1000 events/sec at the resonance frequency. Essentially, all of the resonance electrons will be shunted to a detector by applying a potential of about 2 V to a grid at the reaction zone. This technique is expected to produce much higher intensities than conventional photoelectron spectroscopy with resolutions of about 2 meV. The apparatus will be combined with a mass spectrometer to determine the positive ions produced versus the energy state ionized and the lifetime of these ions.

The Deutsche Forschungsgemeinschaft (DFG), FGR's equivalent to the NSF, has given Pollak a grant to develop the PIR technique. The DFG is also supporting him in developing a three meter, high resolution monochromator (for radiation over the 200-2000 Å range) for coupling PIR to the accelerator storage ring "DORIS" being constructed near Hamburg. This will permit tapping the synchrotron radiation continuum as a high intensity ionization source.

Laser Developments - The third group under Schlag is developing dye lasers to replace the arc uv source in the excited state lifetime studies. The increased intensities will permit direct phase shift determination (as opposed to the present single photon counting now being done). They are currently pumping with flash lamps, but plan to convert to nitrogen laser pumping. They hope to obtain a 0.01 Å resolution by coupling a Fabry and Perot Etalon wavelength selector with a Joubin-Yron three meter, high resolution spectrograph. This French spectrograph Schlag says is the best on the market, being very stable. Two main problems they will be addressing in the application of lasers to lifetime studies is electromagnetic radiation shielding and development of electronics for cross correlation analysis of the photodecay from excited states produced by high intensity, nanosecond duration pulses.

The laser group is also studying the effect of placing absorbing species in the laser cavity and the potential of this technique for detection and identification of trace materials. They expect an increase in sensitivity of about 10^5 compared to having the sample outside the cavity.

They are also investigating solid coating for increasing photomultiplier efficiencies over a broad range of frequencies. The object is to coat the photomultiplier with a material having high absorption over a broad range, but which emits only at the frequency where the photomultiplier is most efficient. Sodium salicylate is usually used for this purpose; however, its efficiency has not been well established (reported values range from 0.4 to 0.9). Besides determining its efficiency more accurately, other materials will be investigated, e.g., the meta and para isomers of sodium salicylate.

Prof. Schlag is one of the editors of a new journal entitled Chemical Physics, published bi-monthly by North-Holland, Amsterdam. It was established as a European based equivalent to the Journal of Chemical Physics, primarily to get away from the high publication costs of the latter. He also hopes to be able to host an International Conference on Radiationless Transfer Process about September 1974 in the Munich area.

The JANAF Thermochemical Tables

J. F. Masi

In expanding its responsibilities during the year to include some closely related areas of the engineering sciences, the Directorate of Chemical Sciences has taken under its wing that research effort which produces the well-known JANAF Thermochemical Tables! This project was initiated, under that name, in response to the urgent need of standardized thermodynamic data by the surging national effort in chemical rocket propellants. For the first five years (1959-1964) the Tables were financed entirely by the Defense Advanced Research Projects Agency, and were supported from 1965-1969 by the Air Force Rocket Propulsion Laboratory. When rocket technology entered a declining period, and it was realized that the Tables could serve the needs for similar data in a variety of other aerospace technologies, their support was transferred to AFOSR.

It is appropriate to call attention to some of the reasons for the phenomenal success of the JANAF Thermochemical Tables in achieving, first, the initial limited objective of providing the standard data for the chemical rocket propulsion industry, and later, upon publication, worldwide recognition as thermodynamic reference data of the highest quality and timeliness.

First, and most obvious, there was the selection and continued support of a highly competent evaluation team, themselves engaged in a broad spectrum of thermodynamic research. The personnel of the Thermal Research Laboratory of the Dow Chemical Company, under the direction of Dr. D. R. Stull, then Dr. H. Prophet, and presently Dr. Malcolm Chase, have filled this role to a degree of excellence not likely to be exceeded anywhere. Moreover, the group has heroically remained productive in spite of many battles to retain continuing support, and the actual sharp reduction of funding over the past five years to a barely viable level.

A second important factor is the unusual approach to format, evaluation, and distribution of the Tables, as it has been followed since their inception. The primary distribution is in frequently-issued loose-leaf supplements. Each previously issued table may thus be revised as often as necessary to take account of improved data. Each loose-leaf table is accompanied on its reverse side by a complete explanation of the selection of the key data, together with all references.

Th The third vital distinction of these Tables has been the existence of a continuing cognizant working group composed of technological users of data, thermodynamicists, and government sponsors of both research and development. Independent pre-publication review of the Tables has been an important contribution of some of the members of this group; but its annual technical meetings have resulted in even more far-reaching benefits. Together, the users and generators of data have been able to establish realistic priorities for the species to be included in the Tables; at the same time the course of experimental research has been guided by the demonstration of absence or inadequacy of needed data. For several

reasons, this large interagency/contractor working group has been discontinued. A much smaller group, befitting the reduced levels of funding for both the Tables and the research scientists producing new data, is being formed to continue to provide scrutiny and necessary focussing of the thermodynamic data work being supported by the Directorate of Chemical Sciences, AFOSR.

References:

D.R. Stull and H. Prophet, "JANAF Thermochemical Tables, Second Edition" NSRDS-NBS-37, U. S. Government Printing Office (1971) (Cat. No. c 13.48.37, $9.75)

AFOSR Organometallic Chemistry Research Program, Past and Present

A. J. Matuszko

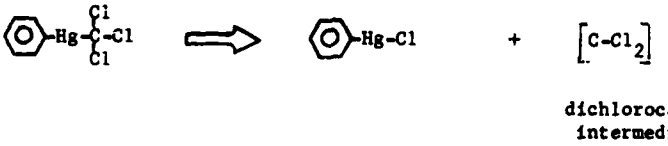
A little over ten years ago, the Chemistry Directorate of AFOSR recognized the growing importance of organometallic chemistry, an area of research which was beginning to receive the attention of a sizeable group of organic, inorganic, and physical chemists in the United States and throughout the world. Although some AFOSR support was directed to a few selective work efforts in the area prior to this time, a concerted effort was made to capitalize on the innovative work being proposed in the process of developing an organometallic chemistry program relevant to the future requirements of the Air Force. Ten years ago, the program was rather small but covered a broad area of the field of organometallic chemistry. In the years that followed, as this area of research grew by leaps and bounds, and other agencies built up programs of their own, we were able to formalize a research program which was specifically attuned to Air Force interests.

The potential uses of organometallics, together with the chemistry resulting from studies of their reactivities and characteristic properties, are many and varied. An important application of the chemistry which comes to mind is in the strengthening of metal to metal bonding adhesives to replace riveting in aircraft structures. An understanding of the chemistry of metal to carbon to metal bonding (an important consideration in organometallic research) provides the pathway for the development of strong, environmentally resistant adhesives. Organometallic catalysts have provided for the synthesis of stereospecific organic polymers, making available polymeric materials with greater resistance to extremes in temperature and pressure. Organometallics are being used as burning regulators in rocket fuels to promote more efficient combustion. Polymer systems with organometallic (or organometalloid) backbones are among the candidates for high temperature and non-flammability applications. Some organometallic compounds are useful for generating reactive intermediates in synthesis, while others are being considered as potential semiconductors, superconductors, or sensors, and as precursors for high purity metals.

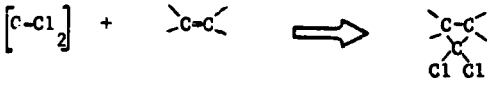
Among the accomplishments from the AFOSR supported research has been the work at Penn State University by Dr. Philip Skell on generating metal atoms and reacting them with organic substances to form organometallic compounds. Using methods developed for producing and studying the properties of atomic carbon species Skell was able to generate metals in their atomic states. A number of metals in the periodic table have been investigated, particularly magnesium, platinum, iron, tungsten aluminum, nickel, cobolt, iron, chromium, silicon, dysprosium, and erbium. The chemistry of these metal atoms was different from that of metal ions in solution or that involving heterogeneous reactions at the surface of the bulk metal. Reactions of the metal atoms with organic compounds resulted in the formation of a large number of previously unavailable organometallic compounds. These compounds could be useful in the preparation of high purity metals for conducting materials, or for the deposition of metallic coatings upon decomposition of the organometallic

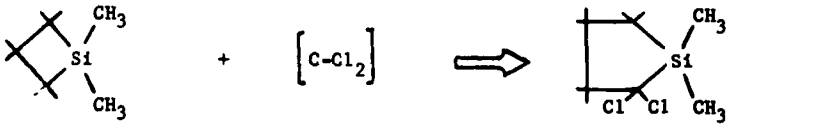
substance. Research is continuing on learning more about the chemistry of these atomic species.

At MIT, Dr. Dietmar Seyferth has been studying methods of generating dihalocarbenes from organomercury compounds. Through decomposition of $C_6H_5HgCX_2Cl$ (where X is chlorine, fluorine or bromine) he has obtained CX_2 intermediates which add across carbon to carbon double bonds to form cyclopropane derivatives and insert into single bonds.



dichlorocarbene intermediate



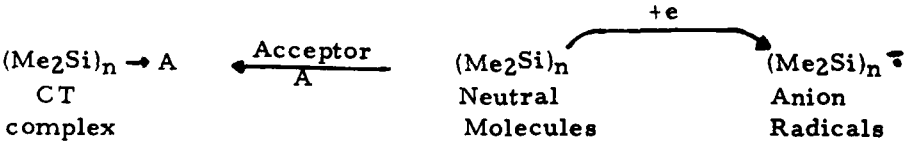


4-membered carbon silicon ring

5-membered carbon-silicon ring

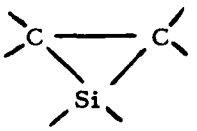
The insertion reactions, particularly those involving diflurocarbene, may be useful in modifying fluorocarbon monomers or fluorocarbon polymers.

At the University of Wisconsin, Dr. Robert West has been carrying out an extensive study of organosilicon chemistry. Of recent interest has been the work on cyclic and bicyclic polysilanes. West and his coworkers have found that these compounds have unique electrical properties and serve as charge transfer agents when paired with organic compounds such as tetracyanoethylene. A study of the properties of these charge transfer



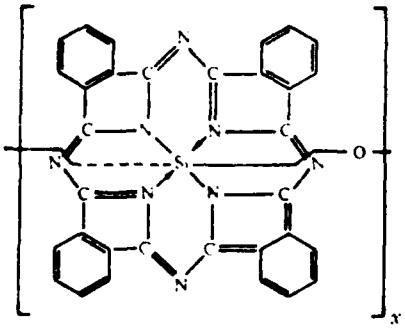
complexes may reveal insight into new semiconducting or superconducting materials.

In this same organosilicon area, Dr. Seyferth at MIT has successfully prepared for the first time silacyclopropanes. He is in the process of



studying the chemistry of these compounds. By varying the organic substituents on the silicon it is possible to readily make any number of organosilicon derivatives. In addition to the work, research recently started with Dr. William Weber at the University of Southern California involves the synthesis and properties of organosilicon heterocyclic compounds.

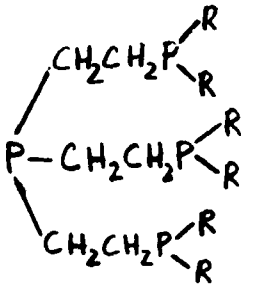
Some years ago AFOSR supported work at Case Institute under the direction of Dr. Malcolm Kenney which involved a study of the synthesis and properties of a new series of high temperature compounds called phthalocyaninosiloxanes. These were hexacoordinate silicon derivatives which exhibited high thermal stability. Since these materials were

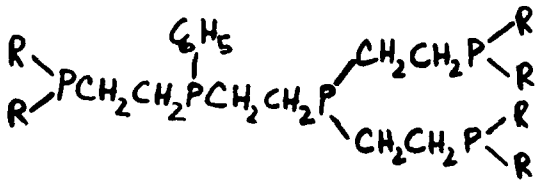


Unit of Phthalocyaninosiloxane Polymer

insoluble in most solvents they seemed to have limited Air Force application and the work was not continued by AFOSR. However, the Navy Bureau of Ships became interested in the compounds for some of their high temperature applications and continued the research with Kenney.

Dr. Bruce King at the University of Georgia has synthesized a variety of organometallic and organometalloid compounds. He has recently synthesized a series of trivalent organophosphorus compounds, some of

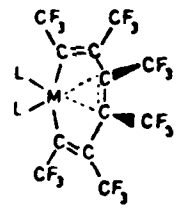




which are quite stable. These compounds may be useful as antioxidant additives in pentaerythrytolester lubricants.

Research at General Electric under Dr. Leonard Interrante on properties of metal to metal bonded organometallics has been yielding information pertaining to new unidirectional conducting systems. Application of pressure shortens the metal to metal bond distance and changes the conductivity. Conductivity also depends on the organic side group bonded to the metal. The results obtained should be useful in the development of new electromagnetic materials for the Air Force.

Dr. Gordon Stone of Bristol University has been devising new synthetic routes to metal cluster compounds containing three or more metals, and studying the properties of various ligands attached to the metals. His objectives have been to discover new chemical structures expected to display unusual properties (thermal, optical, conductivity), and to discover chemical systems which will increase the understanding of mechanisms of homogeneous and heterogeneous catalysis. Among new metal complexes discovered and fully characterized is the stucture shown below.



M = Ni, L = $AsMe_2Ph$
M = Ni, L = $P(OMe)_3$
M = Pt, L_2 = diphos

In research performed at Texas A&M University on new organolanthanides and organoactinides, Dr. Minoru Tsutsui is investigating compounds in which the f orbitals contribute significantly to the bond energy (f-penetration complexes). Of specific interest are the chemical and physical properties of species involving covalent bonding between the metal and organic moiety, together with investigations of their catalytic activity.

Described have been some of the highlights of work in the organometallic area which AFOSR has supported in the past or is presently supporting. Some other research investigators who have been in the program and who have contributed significantly to widening our understanding of organometallic chemistry are Dr. Teddy Taylor of the University of California (San Diego), Dr. Herbert House of MIT, Dr. Larry Dahl of the University of Wisconsin, Dr. Jay Kochi of Indiana University, and Dr. Alan MacDiarmid of the University of Pennsylvania. The results of past and presently support research are providing a base for new developments to serve the future requirements of the Air Force.

Electrochemistry

D. W. Elliott

The state-of-the-art in instrumentation and techniques essentially determine the nature of processes which can be studied and, more importantly, exercise the ability of an investigator to detect experimental deviations from simple models. Examples of the impact of instrumentation and technique improvements upon the field of electrochemistry within the past decade are many. Some examples are: the ability to observe the nature of electrochemically generated species near an electrode surface, kinetic quenching through cryoelectrochemical techniques, development of spectrometers which can scan 3000 Å in milliseconds, allowing spectral monitoring of transient processes, applications of finite difference computational techniques to electrochemical problems which allows numerical solutions to complex electrochemical behavior, linking minicomputers to control and monitor instrumentation resulting in order of magnitude increases in timing, data acquisition, control accuracy, and graphic displays.

At the University of North Carolina, Dr. C. N. Reilley and *Richard Van Duyne have added to the foregoing examples by developing low-temperature electrochemical techniques in their study of the characteristics of electrode reactions in the absence of coupled chemical kinetics.

In the development of the processes, it was necessary for them to design and implement experimental equipment for collection of the data. Among the required equipment was low-temperature electrochemical cells and a variable temperature electrochemical cryostat. The following discussion deals with their development and utilization.

The cells used for all low-temperature voltammetric and transient potential-step experiments are shown in Figures 1 and 2. Both cells were designed with opposed coaxial, working, and reference electrodes surrounded by a platinum coil auxiliary electrode. The cylindrical symmetry of this three-electrode configuration provides uniform current and potential distributions across the surface of the working electrode while the short interelectrode distances result in as small uncompensated and compensated cell resistances as are geometrically possible. Achievement of this nearly ideal electrode geometry for minimizing uncompensated ohmic drop between working and reference electrodes is specially important in low-temperature potentiostatic transient experiments since the solvent-supporting electrolyte media is of considerably higher resistance than in the corresponding ambient temperature situation.

The jacketed low-temperature cell (Figure 1) was used primarily for preliminary work and fixed, low-temperature measurements. The SCE reference electrode contacts the low-temperature test solution through an intermediate non-aqueous salt bridge and a Luggin capillary probe. The intermediate salt bridge serves two functions: protection against

*Now at Northwestern University

contamination of the nonaqueous test solution by water from the reference electrode; and thermal isolation of the SCE from the low-temperature environment. Reference electrode probe-working electrode spacing is adjustable (1 mm is usual), and the spherical joint permits precise electrode alignment. The small volume of the cell (approximately 10 ml) is advantageous in that consumption of difficult to purify nonaqueous solvents is low, and thermal equilibrium is established fairly rapidly. Cell cooling is accomplished by immersion in an open top 4-liter dewar containing a solvent slush bath (dry-ice refrigerant). Cell temperature is monitored by a copper-constantan thermocouple (0 °C reference junction) with read-out to a potentiometer (Rubicon Model 2730) or a stripchart recorder (Sargent Model SR). For experiments conducted in the -60 °C range where solvent slush baths were sometimes inconvenient (or toxic), methanol coolant was circulated through the cell jacket using a thermoregulating bath (Beckman Thermocirculator 181800) fitted with a dry-ice/methanol heat exchanger (Haake Model K-60). A +40 to -59 °C contact thermometer provided 1 °C regulation. Cell-jacket frosting and excessive heat losses to the surroundings were reduced by placing the entire cell assembly with a styrofoam insulating housing.

A variable temperature electrochemical cryostat (Figure 2) was constructed which retains the desirable features of the electrode configuration in the cell of Figure 1. Operation of this cryostat requires only about 4 ml of nonaqueous solvent and has low thermal mass, thus improving its thermal response time. Uniform temperature distribution as well as deaeration of the test solution is accomplished by passing highest purity nitrogen through the long stainless steel hypodermic needle immersed in the solution to be studied. The length of the reference electrode probe is adjusted to provide 1-mm working-reference electrode spacing. The reference electrode junction A consists of a cracked glass tip constructed by fusing a 0.5-mm diameter soft glass rod into a slightly larger hole formed at the tip of the borosilicate glass reference electrode probe. This junction has been found highly effective in preventing water contamination of the nonaqueous test solution while maintaining good electrical contact under low-temperature conditions. A planar platinum working electrode is shown in Figure 2, although a gold or amalgamated platinum electrode could have been used as well. In constructing platinum electrodes, it is important to avoid completely sealing the joint holding the electrode because, when cold, the partial vacuum created will force solvent through the nonvacuum tight borosilicate glass seal around the platinum. This problem is simply avoided by leaving a small hole in the exterior portion of the electrode holder. The vacuum jacketed cryostat dewar B has been strip silvered to facilitate viewing of the electrode arrangement under low-temperature conditions. This is quite valuable when working with a supercooled solvent that may accidentally crystallize or with a marginally soluble supporting electrolyte that may precipitate.

Cooling of the cryostat is achieved by passing compressed, dry nitrogen gas through a copper coil immersed in a liquid nitrogen (LN_2) heat exchanger (4-liter dewar); and then through the vacuum jacketed dewar of the cryostat. The cooling gas flow rate is indicated by a flowmeter

(Gilmont No. 4) located at the cold N_2 outlet and adjusted by means of a back pressure valve to a value slightly in excess of the cooling rate necessary to balance the heat leaks of the cryostat at the lowest control temperature desired. A 24-ohm, vacuum jacketed heater is located in the gas inlet line between the dewar B and the LN_2 heat exchanger. The heater is powered by a 55-watt programmable dc power supply (Kepco Model CK-36-1.5M). The temperature of the cooling gas and, in turn, the cryostat is automatically regulated with a Leeds and Northrup Speedomax W recorder-controller (series 80 C.A.T. proportional controller) equipped with a copper-constantan sensing thermocouple. When the sensing thermocouple, which is located in the cold N_2 gas space surrounding the low-temperature electrochemical cell, indicates a difference between actual gas temperature and controller set point temperature, the C.A.T. controller programs the heater power supply to provide a heater current proportional to the actual set-point temperature difference. This controlling action continues until the set point temperature is reached, at which point a steady state is established where heat and refrigeration fluxes just balance. With this system, any temperature in the range 300 to approximately 90 ^{o}K can be set and maintained to 0.2 ^{o}C. A second thermocouple immersed in the test solution is used to measure the actual electrochemical cell temperature. The dynamic behavior of this controller-cryostat system is such that a 150 ^{o}K temperature excursion from thermal equilibrium at 300 ^{o}K to thermal equilibrium at 150 ^{o}K can be made in approximately 20 minutes and 10 ^{o}K changes can be made from one equilibrium set-point temperature to another in as little as 6-7 minutes.

It is this type of ingenuity that advances the "state-of-the-art" and makes what may appear to be just ordinary, but what could turn out to be significant contributions to the electrochemical field and to other areas of science.

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R. P. Van Duyne and C.N. Reilley, "Characteristics of Electrode Reactions in the Absence of Coupled Chemical Kinetics", Analytical Chemistry, Vol. 44, No. 1, June 1972

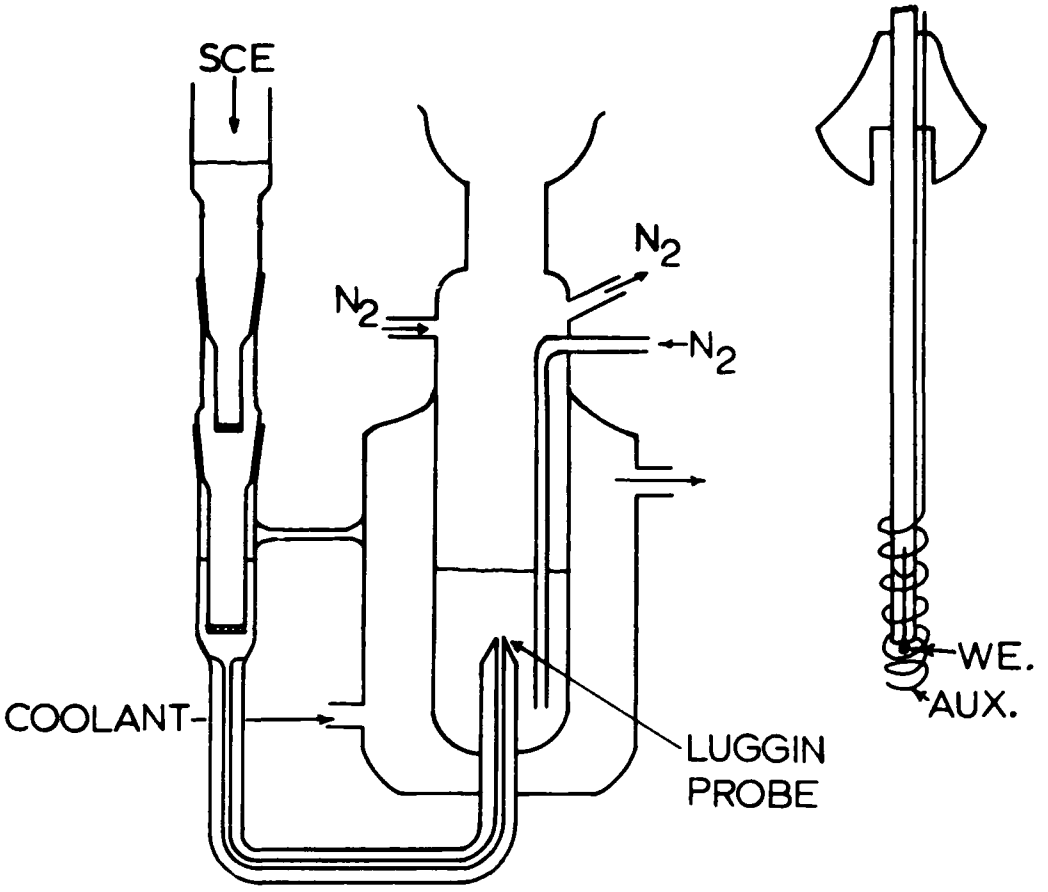
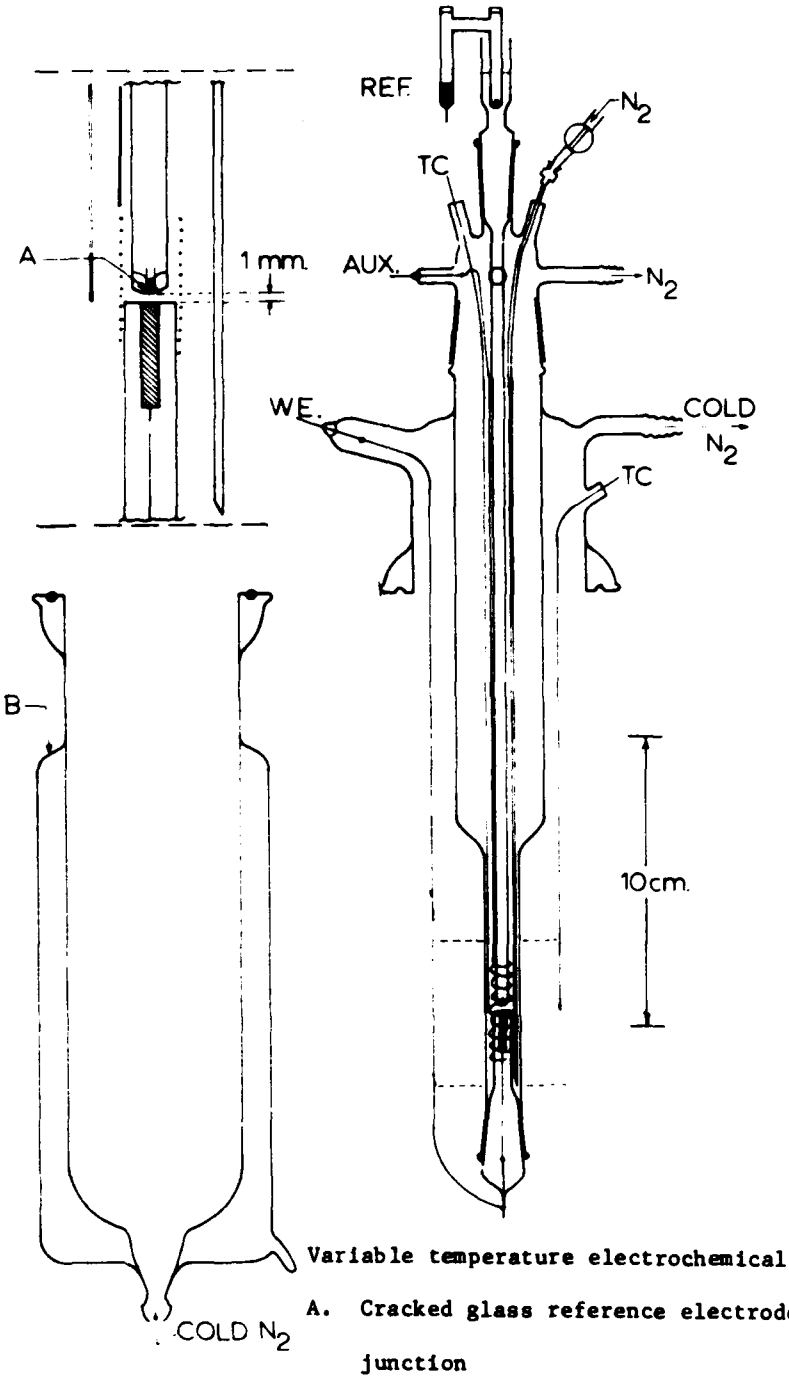


Fig. 1

Low-temperature electrochemical cell for fixed temperature measurements.



Variable temperature electrochemical cryostat.

A. Cracked glass reference electrode-saltbridge junction

B. Vacuum jacketed dewar strip silvered for easy viewing of the electrode arrangement

TC. Copper-constantan thermocouples

REF. SCE.

Fig. 2

Surface Chemistry

D. W. Elliott

Surface chemistry has been in a stage of rapid development in recent years. This progress is due, in part, to the application of experimental techniques which can probe the nature of surfaces on an atomic scale. The need for small devices with large surface volume ratio in many fields of science and technology, increased research activity in aerospace science, solid state, biochemistry, and high temperature chemistry gave further impetus to surface science progress. Our understanding of the properties of surfaces has been hampered by the lack of knowledge of surface structure. Experimental and theoretical studies of surface phase transformations and the structure of adsorbed gases on solid surfaces shed new light on the relationship between surface structure and the nature of surface reactions. Experimental techniques such as low energy electron diffraction (LEED), field ion and field emission microscopy, electron spectroscopy, Auger spectroscopy, molecular beam scattering studies from surfaces, and ellipsometry all provide valuable information about the physical-chemical properties of surfaces and the interaction of gases with surfaces. From the application of all of the techniques to the investigation of well defined surfaces and from theoretical studies a new physical picture of the atomic properties of surfaces emerges.

There is little question that one of the most important current areas of research is the general area of surface and interface science. It has direct and crucial applications to the fields of catalysis and materials sciences. This includes chemisorption, heterogeneous catalysis, catalysis poisoning, corrosion, lubrication, friction and wear adhesion, protective coatings, alloying, mechanism of epitaxial growth, segregation of impurities at interfaces, and synthesis of materials, to mention a few. Also involved is its application to a variety of important technological problems which includes various Air Force problems dealing with propulsion, such as combustion efficiency, energy control, chemical emissions and their identification and control.

To aid in unravelling the complex puzzle of surface phenomena, the Chemistry Directorate has been supporting several outstanding investigators in the surface chemistry and catalysis area. Some of the contributions made by these scientists are cited.

At the University of Illinois, Professor Gert Ehrlich and his research group have been making observations on photo-stimulated field emission and have come up with a new absolute method for determining work functions.

One of their interests has been to establish the nature and extent of structural selectivity in chemisorption. In this regard, the most interesting system has proven to be tungsten; in their past studies its (110) plane has been found to behave in most peculiar ways, showing little reactivity toward nitrogen or hydrogen. The present effort has been directed toward establishing the behavior of hydrogen on the (110) under unequivocal conditions. One of the major problems in establishing chemical behavior on unreactive surfaces, such as the (110) plane, is the difficulty of characterizing the structure and chemical composition of the interface. Unless this can be accomplished with atomic detail, the results of measurements on such surfaces are bound to be obscured by occasional intrusions of chemical and structural impurities. They have now been able to carry out studies on well defined (110) planes by using field evaporation methods.

Field evaporation at low temperatures produces a surface with the same low impurity content as the bulk. Moreover, they are able to characterize the

extent of an individual plane by field emission alone. Field evaporation is carried out in very small increments by raising the applied voltage one volt at a time. The emission characteristics from a small region of the emitter, 20 A in diameter, are then measured as the emitter is tilted off axis. It is thus possible to obtain a profile of the emission as a function of the distance from the center of the plane, as shown in Fig. 1. The minimum in the current through the probe hole fixes the middle of the (110). As one moves away from the center of the plane, shoulders become apparent; these are indicative of the edges of the (110). From such an angular profile of the field emission current, one is able to define the size of the perfect (110), and to establish that subsequent measurements are, in fact, typical of an ideal surface, unmarred by any undesirable structural features.

Measurements of hydrogen adsorption on these ideal surfaces have proved most interesting. At room temperature the behavior is much like that already found earlier on tips produced by thermal annealing, tips whose surfaces cannot be as well documented. On first exposure to hydrogen at 300°K, little happens on the (110), even though the work function of the tip as a whole increases significantly. This suggests that the (110) is relatively unreactive in dissociating the hydrogen molecule. More extensive measurements have been made at 77°K, where these effects are even more startling. This is demonstrated in Fig. 2. When hydrogen is first added to the system, a small but significant rise in the work function is apparent. Further additions of hydrogen do not change the emission characteristics until the rest of the surface is fully covered; only then does the work function of the (110) change, the change occurring in the opposite direction from what happens on the rest of the emitter. It has been possible to show that the initial rise in the work function is not characteristic of the (110), but comes from the edges of the plane. Presumably, the edges are able to dissociate hydrogen and on adsorption increase their work function; this change in the emission characteristics of the edges is then reflected to a lesser extent in the center as well. That this is the correct explanation, and that there is no adsorption on the (110) plane itself, is shown by measurements on larger surfaces, in Fig. 3. The edges are now much further away from the region in the center which is being sampled by the probe hole. Under these conditions there is essentially no change on exposure to hydrogen until the remainder of the emitter is filled with adsorbate. At that point adsorption takes place rapidly on the (110), and so far, they have not been able to suppress this delayed adsorption by going to lower temperatures.

The mechanism of the delayed filling of the (110) plane has not yet emerged clearly. The most likely explanation is that filling of this plane occurs by surface diffusion from adjacent areas. Just recently, moreover, they have found that on field evaporated surfaces an additional state of binding appears just prior to the filling of the (110) surface. This could very well be a precursor state involved in transporting the hydrogen to the dissociation site. Only further experiments will establish this.

Even now, however, their observations provide some important insights into a different but related problem, the work function of the (110). For a long time there has been a discrepancy between values found by field emission and other, more macroscopic methods. The latter converged on a work function of 5.4 eV, the former on 6.0 eV. The differences were initially attributed to the greater structural perfection achieved in the field emission microscope. This state of affairs was disturbed, however, when some investigators reported values as high as 7 eV from field emission studies, and it became clear that in field emission the effects of the planes surrounding the (110) were far from negligible. Recently, measurements have been made, again by field emission methods, giving work function values quite close to 5 eV. In these studies the possible

perturbing effects of the periphery were again not directly explored, and there is still a considerable element of doubt about the actual value of this important parameter.

Ehrlich and his group have measured the work function of the (110), using Fowler-Nordheim plots, as a function of the plane size. For small planes they expect to encounter difficulties because of contributions from the edges. For large planes they expect problems because the field at the center of the plane will have dropped significantly below what it is at the edges. They, however, are able to avoid both difficulties by making measurements just at that size at which the edge effects have become unimportant. The size appropriate to this is determined directly, by introducing hydrogen. If there is no change detected in the emission properties of the (110) after hydrogen adsorption on the rest of the tip, raising the average work function by 0.4 eV, they know that the periphery no longer contributes to the probe hole current. In this way, they have established that the work function of the (110) surface is actually 5.45 eV, in excellent agreement with the best measurements on macroscopic surfaces. This is valuable not only for establishing the reliability of field emission methods in general, but it also provides one of the important parameters for evaluating adsorption studies.

One of the more exciting finds of the past year was that of Dr. Ted Beck at Flow Research, Inc., who has been studying crack propagation by an electrochemical technique. He is performing fast fracture experiments on titanium metal under controlled electrochemical conditions which resulted in the discovery that the formation of salt films could be the answer.

Titanium is a metal high on the electromotive series, and it should be very active. It is well known though that titanium is one of the more corrosion resistant metals owing to a spontaneously-formed protective oxide skin. <u>But it has an Achilles heel</u>. Titanium structures have failed catastrophically by stress corrosion cracking, crevice corrosion, and pitting corrosion. What are the conditions under which the protective skin breaks down, or scratches heal, and how fast, and what are the mechanisms? These are the questions to which Dr. Beck has addressed his research program.

The pieces of the titanium repassivation puzzle have now been fit into a self-consistent quantitative picture. The sequence of events, from the moment of formation of new surface and contact with the electrolyte, to steady-state passivity, is indicated in Fig. 4. It can be summarized as follows:

> Initial simultaneous anodic and cathodic current densities are large, driving the surface to a mixed potential little influenced by the applied potential. Cathodically generated hydrogen diffuses into the metal. Anodically formed Ti^{3+} goes into solution. The titanium salt with the solution anion builds up to a critical supersaturation adjacent to the surface, and precipitation is initiated. The surface concentration prior to precipitation is determined by the Sand equation for unsteady-state diffusion of the titanium salt away from the surface. Growth of the resistive salt layer causes a passivation as described by W. J. Muller, in the 1920's and 30's, for more common metals.

Water diffuses through the salt layer and nucleation of oxide patches begins on the metal surface as the corrosion rate is retarded by the salt layer. Two-dimensional nucleation and growth of the oxide patches occurs as described by Fleischmann and Thirsk kinetics. The growth rate at the edge of the patches is limited by diffusion of water through the salt layer. As the first layer of oxide is completed, the rate of formation of Ti^{3+} ion decreases further and the salt film dissolves. The oxide film thickens by high-field conduction. A steady state oxide film thickness is ultimately achieved at about 10^4 seconds from fracture.

During the past year, effort was concentrated on understanding the formation and properties of salt layers. Anodic dissolution experiments were carried out with titanium, copper, and silver in strong mineral acids, extending the W. J. Muller technique to higher current densities and shorter times of salt-film passivation.

New experiments with notched wire specimens of titanium with short luggin capillary to specimen spacing allowed initial anodic current densities of over 100 A/cm^2. Results clearly showed that the initial passivation was due to an anodic process and that it could be attributed to salt films.

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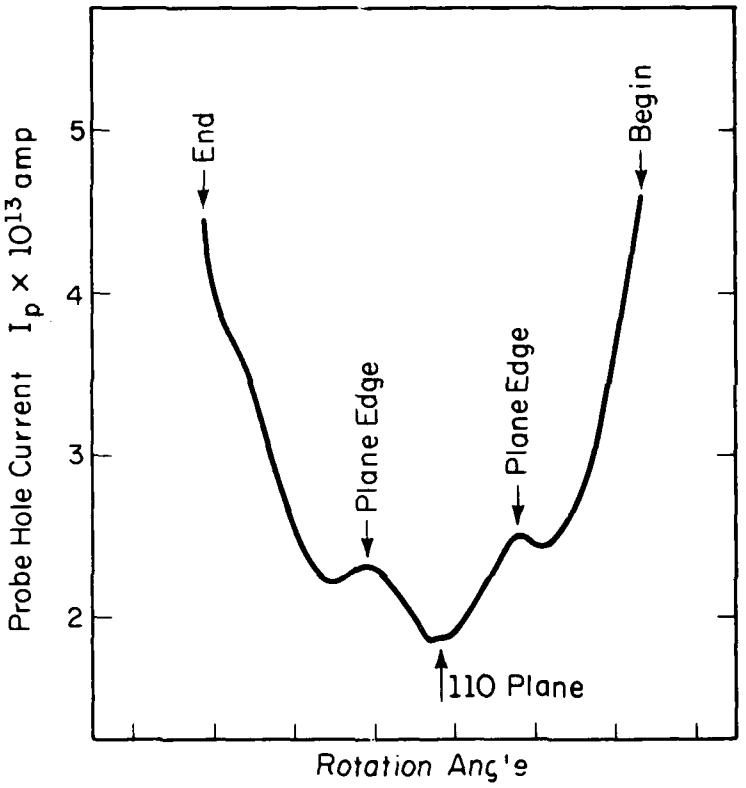

Fig. 1 Probe hole current from [110] oriented emitter at different angles to the [110]. Local maxima reveal the edges of the central (110) plane.

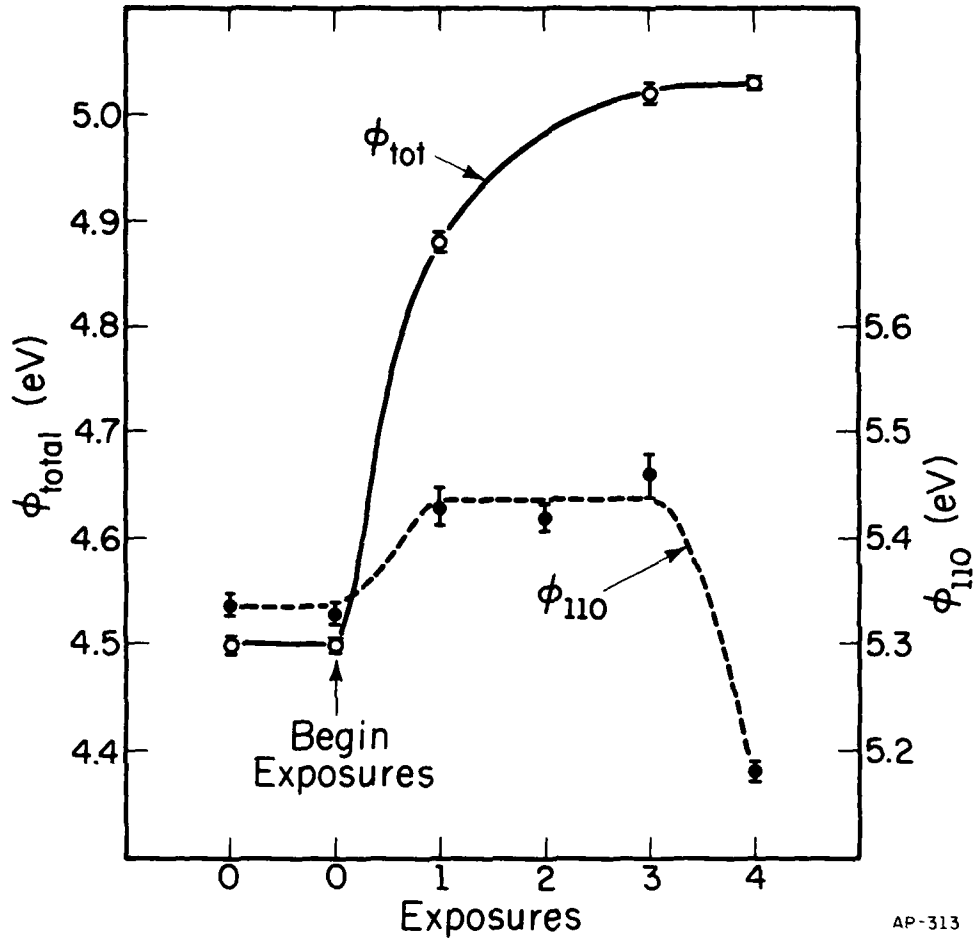

Fig. 2 Adsorption of H_2 on a small (110) plane of tungsten at 77°K. Extent of adsorption is generally proportional to the change in the work function ϕ.

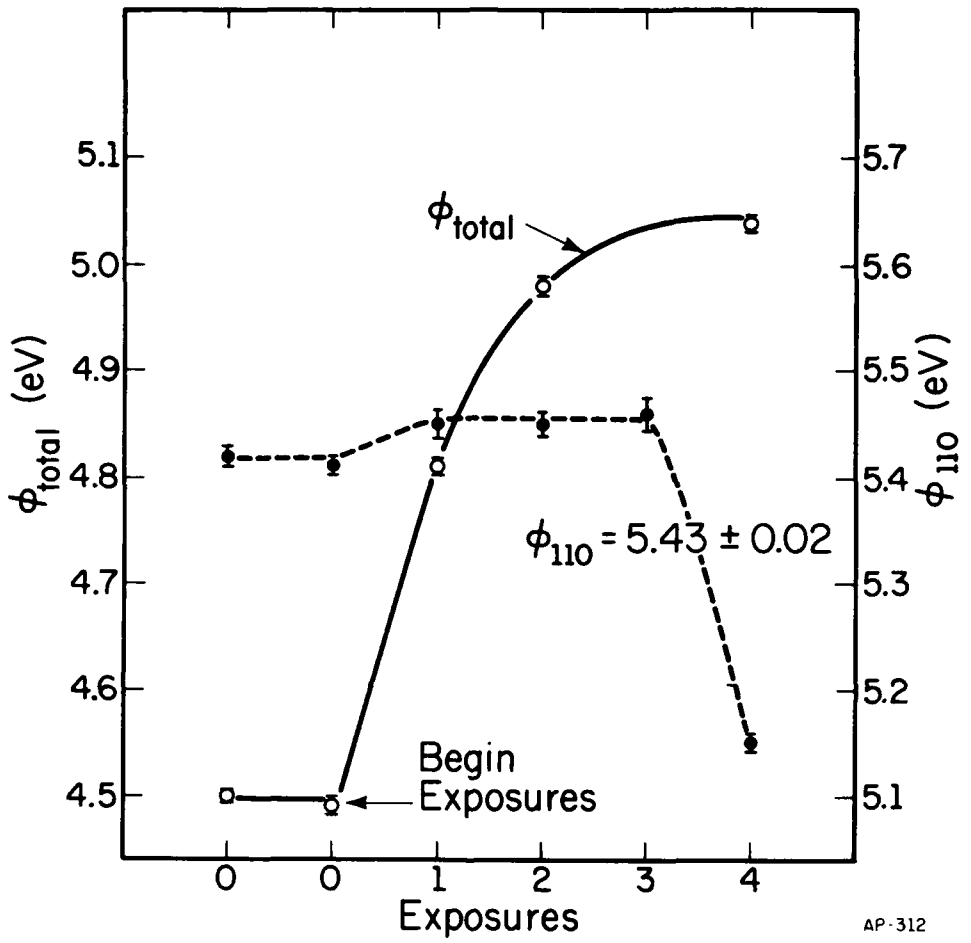

Fig. 3 H_2 adsorption on a large (110) plane of tungsten at 77°K. Changes in the work function of the (110) are within the limit of error.

Time (Sec) →

$O(10^{-3})$	$O(10^{-1})$	$O(10^{4})$
The reactions, 1. $Ti \rightarrow Ti^{3+} + 3e$ and 2. $H^{+} + e \rightarrow H$ occur at a high rate giving a mixed potential.	salt precipitates slowing reactions 1. and 2. Water diffuses through the salt film giving 3. $Ti + 2H_2O \rightarrow TiO_2 + 4H^{+} + 4e$. oxide patches grow and merge	salt film dissolves Oxide film grows by high-field conduction	Steady state oxide thickness achieved

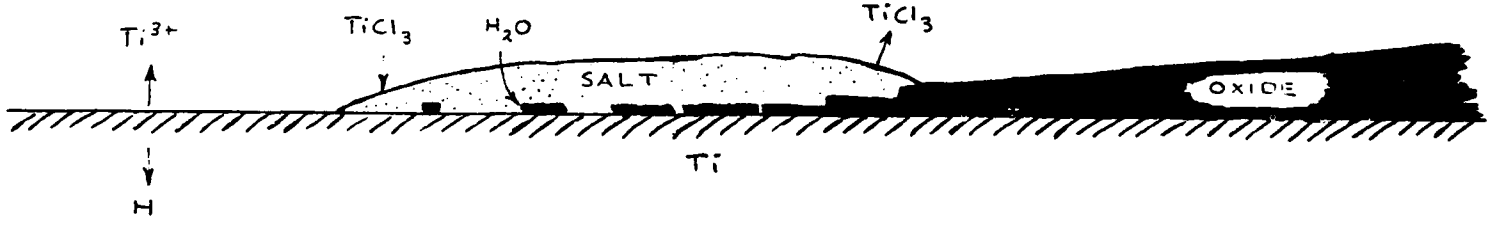

Fig. 4. Time sequence of events after exposure of new titanium surface to HCl electrolyte.

FY 73 Chemistry Program Statistics

(1 July 1972 to 30 June 1973)

	Number
New Work Efforts	15
Renewal Efforts	45
Continuing Efforts	19
Completed Efforts	17
Number of Active Efforts (as of 30 June 1973)	79
FY 1973 Monies Committed	$2,510K

Proposal Action

New Proposals Received	144
New Proposals Declined or Withdrawn	125
New Proposals, Funded in FY 73	17

CHEMISTRY ANNUAL BUDGET FOR PAST TEN YEARS

FY	Expenditures (Thousands)
64	$2,959
65	3,356
66	3,475
67	3,480
68	3,329
69	3,338
70	3,169
71	3,205
72	3,210
73	2,512

PUBLICATIONS RECEIVED DURING FY 1973 ON PROJECTS EXPIRED DURING PRIOR YEARS

Borowitz, I. J.
Yeshiva University
New York, New York
AF-AFOSR-1170-67

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Washington State University
Pullman, Washington
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Crowell, A. D.
University of Vermont
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Dewar, M. J. S.
University of Texas
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F44620-70-C-0121

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Duncan, J. F.
Victoria University of Wellington
Wellington, New Zealand
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University of Notre Dame
Notre Dame, Indiana
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Pasadena, California
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Pennsylvania State University
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AF-AFOSR-0907-67

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University of Western Australia
Nedlands, Australia
AF-AFOSR-1806-69

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AF-AFOSR-1409-68

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Overend, J.
University of Minnesota
Minneapolis, Minnesota
AF-AFOSR-0570-67

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Seyferth, D.
Massachusetts Institute of Technology
Cambridge, Massachusetts
AF-AFOSR-1970-71

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Trueblood, K. N.
University of California
Los Angeles, California
AF-49/638/00719

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Research Efforts (as of 30 June 73)

ALPHABETICAL BY PRINCIPAL INVESTIGATOR

Adsorption on Molecular Solids	Arthur W. Adamson Department of Chemistry University of Southern California Los Angeles, California 90007
Elementary Reactions Involved in the Upper Atmosphere	Edward J. Bair Department of Chemistry Indiana University Bloomington, Indiana 47401
Combustion Analysis and the Chemistry of Flames	Kyle D. Bayes Department of Chemistry University of California Los Angeles, California 90024
Microwave Spectroscopy of Boron Compounds Related to High Temperature Polymers	Robert A. Beaudet Department of Chemistry University of Southern California Los Angeles, California 90007
Reactions and Electrochemical Kinetics of Newly Generated Metal Surfaces	T. R. Beck Flow Research, Inc. 1819 S. Central Ave. Suite 72 Kent, Washington 98031
Chemical Laser Studies of Chemical Reaction Dynamics	M. J. Berry Department of Chemistry University of Wisconsin Madison, Wisconsin 53706
Gordon Research Conferences on Inorganic Chemistry	R. J. Bertolacini Department of Chemistry University of Rhode Island Kingston, Rhode Island 02881
The Chemistry of Image Forming Reactions and Sensitizing Dyes for Photographic Systems	George R. Bird Department of Chemistry Rutgers University New Brunswick, New Jersey 08903
Investigation of Electronic Structure by Scattering Techniques	Russell A. Bonham Department of Chemistry Indiana University Bloomington, Indiana 47401

Stabilized Detonation Wave Chemical Laser Systems	J. Ray Bowen Department of Chemical Engineering University of Wisconsin Madison, Wisconsin 53706
Electrochemistry of Hydrazine-Hydrazine Azide Mixtures	Charles T. Brown Chemical Sciences Section United Aircraft Research Labs East Hartford, Conn. 06108
The Physical and Structural Properties of Liquid Crystals and Their Potential as Detectors	Glenn H. Brown Department of Chemistry Kent State University Kent, Ohio 44240
Solid Electrode Studies Related to Corrosion Prevention, Fuel Cells & Batteries	Stanley Bruckenstein Department of Chemistry State University of New York Buffalo, New York 14214
Gordon Research Conference on Electrochemistry	Stanley Bruckenstein Department of Chemistry State University of New York Buffalo, New York 14214
Kinetics of Association-Dissociation Reactions & Energy Transfer in Diatomic Molecules	George Burns Department of Chemistry University of Toronto Toronto, Canada
Novel Chemical Laser Systems	Terrill A. Cool Laboratory of Plasma Studies Cornell University Ithaca, New York 14850
Spectroscopic Investigations of Luminescent Transition Metal Complexes in Magnetic & Electric Fields	Glenn A. Crosby Department of Chemistry Washington State University Pullman, Washington 99163
Organometallic Energy Transfer Materials for Fuel Cells	Raymond E. Dessy Department of Chemistry Virginia Polytechnic Institute Blacksburg, Virginia 24061
Prediction of Properties and Behavior of Materials	Michael J. S. Dewar Department of Chemistry University of Texas Austin, Texas 78712

Scientific Evaluation of Proposed Chemical Research with Potential US Air Force Interests	Joseph E. Earley Department of Chemistry Georgetown University Washington, D.C. 20007
Reactivity Patterns Characteristic of Lighter Metallic Elements (Titanium)	Joseph E. Earley Department of Chemistry Georgetown University Washington, D.C. 20007
Controlled Reactivity in Some Unstable Inorganic Reagents	John O. Edwards Department of Chemistry Brown University Providence, R.I. 02912
Semiconductor Surface Chemistry	Gert Ehrlich Coordinated Science Laboratory University of Illinois Urbana, Illinois 61801
Rapid Reactions in Photographic Chemistry	Edward M. Eyring Department of Chemistry University of Utah Salt Lake City, Utah 84112
Molecular Beam Investigation of Energy Transfer and Chemical Reactivity	John B. Fenn Department of Engineering and Applied Science Yale University New Haven, Connecticut 06520
The Structure and Properties of Polymeric Materials	Paul J. Flory Department of Chemistry Stanford University Stanford, California 94305
Ionization Processes Relevant to the Formation of New Materials	Harlan L. Goering Department of Chemistry University of Wisconsin Madison, Wisconsin 53706
Structure and Properties of Glasses and Liquids	Martin Goldstein Belfer Graduate School of Science Yeshiva University New York, New York 10033
Synthesis & Polymerization of Flurobicyclobutanes to Chemically, Thermally & Dimensionally Stable Polymers	H. K. Hall, Jr. Department of Chemistry University of Arizona Tucson, Arizona 85721

Chemical Reactions Induced by Ultraviolet and Ionizing Radiation	George S. Hammond Department of Chemistry University of California Santa Cruz, California 95060
The Nature of Non-Stoichiometric Solids-Structure, Texture, Thermodynamic and Magnetic Properties	Bruce G. Hyde & B. N. Figgis Department of Physical Chemistry University of Western Australia Nedlands, W.A , Australia
The Solid-State Properties of Transition Metal Complexes	Leonard V. Interrante Physical Chemistry Laboratory General Electric Co. Research & Development Center Schenectady, New York 12301
Collisional Energy Transfer & Other Topics Related to Gas Laser Mechanisms	Ali Javan Department of Physics Massachusetts Inst of Tech Cambridge, Massachusetts 02139
High-Pressure Nuclear Magnetic Resonance Relaxation Study of Supercritical Dense Fluids	Jiri Jonas Department of Chemistry University of Illinois Urbana, Illinois 61801
Effect of Structure on the Physical Properties of Polymers	Frank E. Karasz Polymer Science and Engineering University of Massachusetts Amherst, Massachusetts 01002
Structure & Mechanism Studies of High Conductivity Solid Ionic Conductors	John S. Kasper & Walter Roth Physical Chemistry Laboratory General Electric Co. Research & Development Center Schenectady, New York 12301
Transition Metal and Lanthanide Compounds as Fuel Cell Additives, Superconductors, and Laser Materials	R. Bruce King Department of Chemistry University of Georgia Athens, Georgia 30601
Theories of Energy Disposal in Chemical Reactions	Aron Kupperman Division of Chemistry & Chemical Engineering California Institute of Tech. Pasadena, California 91109

Inorganic Photoelectron Spectroscopy, Mass Spectrometry, and Thermochemistry Related to Fuels and Polymers	M. F. Lappert & J. B. Pedley Department of Chemistry University of Sussex Brighton BN1 9QJ Sussex, England
Energy and Chemical Change - Energy Disposal and Energy Requirements of Chemical Reactions	Raphael D. Levine Department of Chemistry Ohio State University Columbus, Ohio 43212
The Chemistry of Materials Under Extreme Environmental Conditions	Willard F. Libby Department of Chemistry University of California Los Angeles, California 90024
Stable Silicon Compounds of Unusual Valence Related to the Synthesis of Improved Polymers	Alan C. MacDiarmid Department of Chemistry University of Pennsylvania Philadelphia, Pennsylvania 19104
Structure & Properties of Glasses	Pedro B. Macedo & T. A. Litovitz Department of Physics Catholic University of America Washington, D.C. 20017
Structure and Properties of Glasses	John D. Mackenzie Department of Chemistry University of California Los Angeles, California 90024
Molecular Basis for Liquid Crystal Field Effects Related to Displays	J. David Margerum Photochemistry Section Hughes Research Laboratories Malibu, California 90265
Fast Kinetic Methods Applicable to Trace Chemical Analysis and Detection	Dale W. Margerum & Harry Pardue Department of Chemistry Purdue Research Foundation Lafayette, Indiana 47907
The Reactivity and Structure of Solid Surfaces	Robert P. Merrill Department of Chemical Engineering University of California Berkeley, California 94720

Quantum Theoretical Studies of Gas-Solid Interactions	R. P. Messmer Physical Chemistry Laboratory General Electric Co. Research & Development Center Schenectady, New York 12301
Electrochemical Processes Associated with Energy Transfer	R. W. Murray & C. N. Reilley Department of Chemistry University of North Carolina Chapel Hill, North Carolina 27514
Electronic and Magnetic Properties of High Temperature Electrolytes	Norman H. Nachtrieb Department of Chemistry University of Chicago Chicago, Illinois 60637
Synthesis and Properties of Interlocking Ring Compounds	Melvin S. Newman Department of Chemistry Ohio State University Columbus, Ohio 43212
Electrochemical Studies in Aluminum Chloride Melts	Robert A. Osteryoung Department of Chemistry Colorado State University Fort Collins, Colorado 80521
Gas-Phase Reactions of Atoms, Ions, and Molecules Related to Upper Atmosphere Chemistry	Leon F. Phillips Department of Chemistry University of Canterbury Christchurch, New Zealand
Chemical Lasers, Ultrarapid Scan Infrared Studies & Laser-Induced Kinetic Processes	George C. Pimentel Department of Chemistry University of California Berkeley, California 94720
Studies of the Properties of Selected Chemical Compounds for Preparation of New Materials	Michael T. Pope Department of Chemistry Georgetown University Washington, D.C. 20007
Collisional Molecular Energy Transfer Characteristic of Combustion	B. S. Rabinovitch Department of Chemistry University of Washington Seattle, Washington 98105
Experimental & Theoretical Studies in Photochemistry	Stuart A. Rice Department of Chemistry University of Chicago Chicago, Illinois 60637

High Energy Chemical Reactivity	John W. Root Department of Chemistry University of California Davis, California 95616
Molecular Processes Controlling Energy Transfer, Storage and Release	Edward W. Schlag Institute for Physical Chemistry Technical University, Munich Munich, Germany
Highly Halogenated Organic and Organometallic Materials	Dietmar Seyferth Department of Chemistry Massachusetts Institute of Tech. Cambridge, Massachusetts 02139
Molecular Energy Transfer by Collisional Processes Characteristic of Gas Lasers	Hyung Kyu Shin Department of Chemistry University of Nevada Reno, Nevada 89507
Properties and Reactions of Atomic Species Generated at High Temperatures	P. S. Skell Department of Chemistry Pennsylvania State University University Park, Pa. 16802
Photochemical Addition of Benzene to Unsaturated Materials	Ringaswamy Srinivasan IBM Corporation T. J. Watson Research Center Yorktown Heights, N. Y. 10598
Molecular Deactivation Processes in Visible Chemical Laser Systems	Jeffrey I. Steinfeld Department of Chemistry M.I.T. Cambridge, Mass. 02139
Solute-Solvent Interactions and Preferential Solvation Related to Electrochemical Power Sources-An NMR Study	Thomas R. Stengle Department of Chemistry University of Massachusetts Amherst, Massachusetts 01002
Transition Metal Compounds with Potential Electronic and Radiation Resistant Properties	F. G. A. Stone Department of Chemistry University of Bristol Bristol, England
Chemical Kinetics of Some Elementary Reactions of Oxygen Atoms	R. B. Timmons Department of Chemistry Catholic University of America Washington, D.C. 20017

New Organolanthanides and Organo-actinides Related to Catalysis	Minoru Tsutsui Department of Chemistry Texas A&M Research Foundation College Station, Texas 77843
Structural and Dynamic Studies of Materials Possessing High Energy Content	Nicholas J. Turro Department of Chemistry Columbia University New York, New York 10027
Applied Quantum Chemistry of Nonmetallic Materials	John R. Van Wazer Department of Chemistry Vanderbilt University Nashville, Tennessee 37203
Unsaturated Organosilicon Heterocycles	W. P. Weber Department of Chemistry University of Southern California Los Angeles, California 90007
Structure and Properties of High Temperature Materials	William Weltner, Jr. Department of Chemistry University of Florida Gainesville, Florida 32601
Chemical Reactions and Properties of Organosilicon Compounds Related to New Materials	Robert C. West Department of Chemistry University of Wisconsin Madison, Wisconsin 53706
Analysis of the Collisional Redistribution of Molecular Energy in Gases	Lennard Wharton Department of Chemistry University of Chicago Chicago, Illinois 60637
Energies and Conformation of Molecules	Kenneth B. Wiberg Department of Chemistry Yale University New Haven, Connecticut 06520
Gas Phase Spectrometry Methods - Trace Analysis of Elements	James D. Winefordner Department of Chemistry University of Florida Gainesville, Florida 32601
Electrode Mechanisms Using Reflection and Electron Spectroscopy	Nicholas Winograd Department of Chemistry Purdue Research Foundation Lafayette, Indiana 47907

High Temperature Gas-Phase Reactions of Metals

R. N. Zare
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Chemiluminescent Reactions as the Basis for Visible Chemical Lasers

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RESEARCH EFFORTS COMPLETED IN FY 72
(Alphabetical by Principal Investigator)

Microwave Spectroscopy of Boron Compounds Related to High Temperature	Robert A. Beaudet Department of Chemistry Univ. of Southern California Los Angeles, California
Rotating Ring-Disk Studies Applicable to Corrosion Prevention, Fuel Cells, and Batteries	Stanley Bruckenstein Department of Chemistry State Univ of NY at Buffalo
Resonance Spectra of Molecules Related to Laser Materials	Thomas M. Dunn Department of Chemistry University of Michigan Ann Arbor, Michigan
Ultra-Fast Reaction Rates in Solution Related to Electrochemistry and Corrosion	Edward M. Eyring Department of Chemistry University of Utah Salt Lake City, Utah
Stable Silicon Compounds of Unusual Valence Related to the Synthesis of Improved Polymers	Alan G. MacDiarmid Department of Chemistry Univ of Pennsylvania Philadelphia, Pennsylvania
Chemistry of Photopolymer Light-Sensitive Systems Relevant to Radar and Other Displays	J. David Margerum Explonatory Studies Dept. Hughes Research Laboratories Malibu, California
Adsorption of Molecules at the Electrodes of Batteries and Fuel Cells	David M. Mohilner Department of Chemistry Colorado State University Fort Collins, Colorado
Fundamental Studies of Electrochemical Processes	R. W. Murray and C. N. Reilley Department of Chemistry Univ of North Carolina Chapel Hill, North Carolina
The Effect of Wavelength on the Degradation of Certain Polymers	W. Albert Noyes, Jr. Department of Chemistry University of Texas Austin, Texas

High Resolution Gas Phase Infrared Absorption Spectra of Simple Gases	John Overend Department of Chemistry University of Minnesota Minneapolis, Minnesota
New High Temperature Fluorocarbons--Their Preparation and Properties	Joseph D. Park Department of Chemistry University of Colorado Boulder, Colorado
The Effect of Atomic Interactions on the Structure and Physical Properties of Fluids	C. J. Rings Division of Chemistry and Chemical Engineering Calif Inst of Technology Pasadena, California
The Structure of Materials and Their Interaction with Radiation	Stuart A. Rice The James Franck Institute University of Chicago Chicago, Illinois
Atomic and Molecular Collision Dynamics in Very High Energy Chemical Systems	John W. Root Department of Chemistry University of California Davis, California
Ion Fragmentation of Organic Materials by Photoionization and Electron Impact	James W. Taylor Department of Chemistry University of Wisconsin Madison, Wisconsin
Oxidative Decomposition of Organic Materials and Reactivity of Organometallic Substances Related to Catalysis	Teddy G. Traylor Department of Chemistry Univ of California (San Diego) La Jolla, California
Gas Phase Spectrometric Analysis of Trace Elements	James D. Winefordner Department of Chemistry University of Florida Gainesville, Florida

Completed Project Summaries

COMPLETED PROJECT SUMMARY

1. TITLE: Microwave Spectroscopy of Boron Compounds Related to High Temperature Polymers and Rubber Catalysts

2. PRINCIPAL INVESTIGATOR: Professor Robert A. Beaudet
Department of Chemistry
University of Southern California
Los Angeles, California

3. INCLUSIVE DATES: 1 June 1965 - 31 October 1971

4. GRANT NOS.: AF-AFOSR-849-65; AF-AFOSR-849-67

5. COSTS AND FY SOURCE: $43,680 FY 65; $47,441 FY 67; $20,088 FY 70; $24,543 FY 71

6. SENIOR RESEARCH PERSONNEL: Dr. E. H. Cohen
Dr. G. L. McKown

7. JUNIOR RESEARCH PERSONNEL: S. C-C. Cheung
L. Li

8. PUBLICATIONS:

"The Microwave Spectrum, Molecular Structure, and Dipole Moment of Dicarbaheptaborane(7)," J. Chem. Phys., 43, 2166 (1965).

"The NMR and Microwave Spectrum of Some Deutero-Derivatives of 2,4-Dicarba Clovoheptaborane(7)," T. Onak, G. B. Dunks, and R. L. Poynter, J. Am. Chem. Soc., 88, 4622 (1966).

"Microwave Spectrum, Vibration-Rotation Interaction, Molecular Structure, and Dipole Moment of 1-Methylpentaborane(9)," E. A. Cohen, J. Chem. Phys., 48, 1220 (1968).

"Improved Sweep Modulator for Microwave Signal Sources," A. Remeikis, R. L. Poynter, and G. R. Steffenson, Rev. Sci. Instru., 38, 1223 (1968).

"The Microwave Spectra, Molecular Structure, and Dipole Moment of Phosphirane," M. T. Bowers, H. Goldwhite, and R. Tang, J. Am. Chem. Soc., 91, 17 (1969).

"CNDO/2 Calculations of Some Carboranes," S. C-C. Cheung, and G. A. Segal, J. Am. Chem. Soc., 92, 4158 (1970).

"Microwave Spectrum, Barriers to Internal Rotation, and Dipole Moments of cis- and trans-Propylene Phosphine," M. T. Bowers, H. Goldwhite, and S. Chan, J. Chem. Phys., 52, 2831 (1970).

"The Skeletal Molecular Structure of Closo-2,3 Dicarbahexaborane(6) from Microwave Spectral Studies," R. L. Poynter, J. Chem. Phys., 53, 1899 (1970).

"Microwave Spectrum of CB_3BF_2," S. C-C. Cheung, J. Mol. Spect., 36, 337 (1970).

"Microwave Spectrum, Structure and Dipole Moment of 2-Carbahexaborane(9) CB_5H_9," S. C-C. Cheung, Inorg. Chem., 10, 1144 (1971).

"Microwave Spectrum, Molecular Structure, and Quadrupole Coupling in 2-Chloro-1,6 Dicarbahexaborane(6)," G. L. McKown, Inorg. Chem., 10, 1350 (1971).

"Microwave Spectroscopy of Boron Compounds Related to High Temperature Polymers and Rubber Catalysts, R. A. Beaudet, Final Technical Report.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Approximately a decade ago, a new class of chemical compounds became of scientific interest. These compounds, called "carboranes," are made up of boron, carbon, and hydrogen atoms. They were particularly interesting because they seem to generally be very stable materials which may be usable in rubbers, plastics, or as catalysts. They occurred in many different molecular shapes which could not be easily predicted from known chemical experience, and the carbon did not obey the rules of organic chemistry in any way. For example, $C_2B_4H_6$ is stable up to 200°C, it has the shape of an octahedron unlike any other compound containing carbon, and the carbon is actually bonded to five other atoms within the molecule. Before the uses of carboranes can be properly assessed, the molecular structures and properties of these compounds must be determined. From these studies we would also hope to be able to better understand chemical bonding and to be able to predict what other new compounds might be possible to synthesize. Molecular structure, including the orientation of the atoms as well as the bond distances and angles, is one of the most useful properties of a chemical compound. Molecular structures are usually determined by one of three means: X-ray diffraction, electron diffraction, or microwave spectroscopy. Each of these methods has its own set of advantages and disadvantages. For example:

a. X-ray diffraction - depends on having a single crystal of material. For liquids and gases, crystals must be prepared at very low temperatures.

b. Electron diffraction - is useful only for small gaseous compounds with a high degree of symmetry.

c. Microwave spectroscopy - must have isotopic species in order to obtain enough information to determine a complete structure.

Since most of the carboranes are volatile liquids and since boron in natural abundance has two isotopes, ^{11}B and ^{10}B in the ratio of 4:1, the structures of the carboranes are very amenable to study by microwave spectroscopy.

The determination of the molecular structure of numerous small carboranes was undertaken. The molecular configurations and structures of the $C_2B_3H_5$, sym-$C_2B_4H_6$ asy-$C_2B_4H_6$, $C_2B_5H_7$, CB_5H_9, CB_5H_7, $C_3B_3H_7$, and $C_4B_2H_6$ frameworks have been determined and published. Carboranes are more complex than most of the molecules that have been previously studied by microwave spectroscopy. Their spectra are usually extremely dense, they are usually very asymmetric molecules, and the spectra are further complicated by the large number of isotopic species present in natural abundance. To aid in the assignments, Dr. Beaudet has further developed means of dealing with complex spectra and obtaining molecular structure when very little prior information is known about the molecule. In the process of the assignments, Dr. Beaudet and his research group have depended very heavily on double resonance methods to sort out the transitions and assign them to the proper quantum levels.

AFOSR Program Manager: Dr. W. L. Ruigh

COMPLETED PROJECT SUMMARY

1. TITLE: Rotating Ring-Disk Studies Applicable to Corrosion Prevention, Fuel Cells, and Batteries

2. PRINCIPAL INVESTIGATOR: Professor Stanley Bruckenstein
Department of Chemistry
State University of New York at Buffalo
Buffalo, New York

3. INCLUSIVE DATES: 1 August 1969 - 31 July 1973

4. GRANT NO.: AFOSR-70-1832

5. COSTS AND FY SOURCE: $48,516 FY 69; $52,303 FY 70;
$63,077 FY 71; $68, 383 FY 72

6. SENIOR RESEARCH PERSONNEL: Dr. M. Petek
Dr. R. J. Smythe
Dr. D. F. Untereker

7. JUNIOR RESEARCH PERSONNEL:

S. H. Cadle	G. A. Martinchek
J. Comeau	T. M. Reidhammer
W. N. Copa	M. Shabrang
D. Cukman	W. G. Sherwood
R. R. Gadde	D. F. Untereker
M. Z. H. Hassan	D. A. Violante
J. A. Kosek	

8. PUBLICATIONS:

"The Use of a Porous Electrode for in situ Mass Spectrometric Determination of Volatile Electrode Reaction Products," S. Bruckenstein and R. R. Gadde, J. Am. Chem. Soc., 93, 793 (1971).

"Rotating Ring-Disk Study of the Reduction of Oxidized Platinum by Mercurous Mercury and Its Adsorption on Reduced Platinum," Stanley Bruckenstein and M. Z. Hassan, Anal. Chem., 43, 928 (1971).

"Rotating Ring-Disk Study of the Underpotential Deposition of Copper at Platinum in 0.5M Hydrochloric Acid," S. H. Cadle and Stanley Bruckenstein, Anal. Chem., 43, 932 (1971).

"Inhibition of Hydrogen Adsorption by Submonolayer Deposition of Metals on Platinum," S. H. Cadle and Stanley Bruckenstein, Anal. Chem., 43, 1858 (1971).

"A Rotating Gold-Ring Disk Study of Sn(II) in 4.0M HCl," V. A. Vicente and Stanley Bruckenstein, Anal. Chem., 44, 297 (1972).

"The Interpretation of Isopotential Points. The Common Intersection in Families of Current-Potential Curves," D. H. Untereker and S. Bruckenstein, Anal. Chem., 44, 1009 (1972).

"Ring Disk Electrode Study of the Reduction of Bismuth on Platinum," S. H. Cadle and S. Bruckenstein, Anal. Chem., 44, 1993 (1972).

"Ring Disk Electrode Study of the Reduction and Oxidation of Bismuth on Gold," S. H. Cadle and S. Bruckenstein, J. Electrochem. Soc., 119, 1166 (1972).

"Electrochemical Study of the Oxidation of Fractional Monolayer Gold Films on Platinum," S. H. Cadle and S. Bruckenstein, Anal. Chem., 44, 2225 (1972).

"Anodic Oxidation of Substituted Methoxyphenols: Mass Spectrometric Identification of Methanol Formed," M. Petek, S. Bruckenstein, B. Feinberg, and R. N. Adams, J. Electroanal. Chem., 42, 397 (1973).

"Ring Disk Study of Thin Mercury Films on Platinum," M. M. Hassan, D. H. Untereker and S. Bruckenstein, J. Electroanal. Chem., 42, 161 (1973).

"A Rotating Ring Disk Electrode Study of the Adsorption of Lead on Gold in 0.5M Potassium Chloride," V. A. Vicente and S. Bruckenstein, Anal. Chem., 40, 2036 (1973).

"An Isotopic Labelling Investigation of the Mechanism of the Electrooxidation of Hydrazine at Platinum," M. Petek and S. Bruckenstein, J. Electroanal. Chem., 47, 329 (1973).

"Ring-Disk Study of the Effect of Trace Chloride Ion in the Anodic Behavior of Gold in 0.2M H_2SO_4," S. H. Cadle and S. Bruckenstein, J. Electroanal. Chem., 48, 325 (1973).

"Ring-Disk Electrode Study of the Anodic Behavior in Gold in 0.2M H_2SO_4," S. H. Cadle and S. Bruckenstein, Anal. Chem., in press.

"A Solution-Redeposition Mechanism for the Roughening of Platinum Electrodes by Cyclic Potential Programs," D. F. Untereker and S. Bruckenstein, J. Electrochem. Soc., in press.

"The Electroreduction of Nitrite in 0.1M $HClO_4$ at Platinum," R. R. Gadde and S. Bruckenstein, J. Electroanal. Chem., in press.

"A Critique of Platinum Surface Roughness Determination by Means of Hydrogen Adsorption," D. F. Untereker and S. Bruckenstein, in preparation.

"Electrochemical Study of the Oxidation of Fractional Monolayer Platinum Films on Gold," D. F. Untereker and S. Bruckenstein, in preparation.

"A Rotating Ring-Disk Study of the Adsorption of Thallium on Gold in 0.5M Potassium Chloride," V. A. Vicente and S. Bruckenstein, in preparation.

"The Interpretation of Ring-Disk Electrode Isopotential Points," D. F. Untereker and S. Bruckenstein, in press.

"Rotating Ring-Disk Studies Applicable to Corrosion Prevention, Fuel Cells, and Batteries," S. Bruckenstein, Final Technical Report.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The goals of this research were to study:

a. the electrochemical deposition and oxidation of submono- and monolayer films of one metal, M, on another, S.

b. the extent and scope of the phenomenon of underpotential deposition, i.e., the deposition of M from a solution of its ions at potentials anodic to the Nernst potential.

c. the role played by adions in these thin films.

d. the effect of partial monolayer coverage and several atom layer coverage on the electrochemical behavior of the substrate, and

e. to develop new experimental methods to study adsorption processes at solid electrodes based on coulometric methods using the ring-disk technique in order to avoid the use of assumed models.

Such studies are of theoretical and practical significance. The electrodeposition of one metal on another is one of the most frequently performed operations in electrochemistry, but there is still no understanding of the interactions that exist at the interface between the electrodeposit and the substrate. Also, the extent to which adsorption of ions and underpotential deposition occur could have great significance in the interpretation of corrosion, battery, and fuel cell studies. The presence of known trace impurities, which unknowingly are adsorbable or depositable, could radically change the results of such studies.

The two substrates used were platinum and gold, since these materials had been extensively investigated by others. During the course of these studies, it became necessary to investigate these substrates further. In the case of platinum, a critical study of the various methods of determining surface roughness using hydrogen adsorption was completed. Also, the mechanism of surface roughening of platinum in acid media under potential cycling conditions was established to be a dissolution-redeposition mechanism. Soluble platinum forms in small quantities when a reduced platinum electrode is oxidized, and also when the oxidized electrode is reduced. At cathodic potentials, the soluble platinum species are redeposited as platinum black. The number of oxygen atoms associated with a platinum atom at potentials just prior to oxygen evolution was shown to be less than two by depositing a thin platinum film on a gold substrate. Analogous studies of thin gold films on platinum yielded the potential at which a 1:1 atom ratio of oxygen to gold exists at a gold electrode. Trace chloride ion is strongly adsorbed on gold in acid media, and strongly effects the behavior of the electrode at anodic potentials. Two kinds of adsorbed chloride ion were identified.

The dissolution rate of gold in 0.2M H_2SO_4 was studied and the formation of Au(I) and Au(III) species established as a function of potential. Appreciable amounts of soluble species are produced during the reduction of the oxidized gold surface layer.

The underpotential deposition of various metals and the adsorption of their ions at potentials anodic to the Nernst potential were shown to occur at gold electrodes for the Sn(II)-Sn couple in 4.0M HCl; the Bi(III)-Bi couple in 0.12M HClO ; and the Pb(II)-Pb and Tl(I)-Tl couples in 0.5M KCl.

Analogous studies were carried out at platinum electrodes for Hg(I)-Hg, Cu(II)-Cu, and Bi(III)-Bi in acid media.

The results of the above studies strongly support the view that as a general phenomenon, uniform coverage of a substrate occurs for the first monolayer of a foreign metal deposit. Furthermore, if the size of the foreign metal atom is less than that of the substrate metals atom, one atom of the foreign

metal deposits for each substrate atom in the surface. If the foreign metal atom is larger than the substrate metal atom, coverages can be calculated with surprising accuracy from estimates of the area occupied on the surface by the foreign metal atom.

The existence of a number of surface compounds (alloys) was established using the isopotential point method. In the cases of Bi and Hg on platinum, it was shown that the equivalent of 4-5 monolayers had to be deposited before bulk alloy formation could occur. This result is in agreement with the view that the phenomena leading to underpotential deposition correspond to extremely strong interactions between foreign metal and surface substrate atoms; until all these interactions are satisfied by the deposition of one or a few layers of metal at underpotential, no bulk alloy formation can occur, nor can diffusion from the surface take place.

As mentioned above, a new method of studying surface compound formation was developed, and is known as the isopotential point technique. It is invaluable in establishing the existence of surface regions of definite stoichiometry and also for establishing the level of adsorbable impurities in solution. It has been extended to the ring-disk electrode, which makes it possible to determine whether soluble species are produced by the processes causing the isopotential point.

During the course of the ring-disk electrode studies, it became necessary to identify and determine certain volatile nonelectroactive species produced or consumed at the electrode surface. The method of electrochemical mass spectroscopy was devised and applied to several complicated electrochemical situations. This technique permits the collection of volatile species present at the surface of an electrode and introduces these species directly into the vacuum inlet system of a mass spectrometer. One application of fuel cell interest involved studying the mechanism of the oxidation of hydrazine at platinum and nickel. In this study it was shown, by the use of ^{15}N-labelled hydrazine, that all the nitrogen atoms in the final nitrogen gas produced by electrochemical oxidation originated from one molecule of hydrazine, contrary to the result found in the homogenous chemical oxidation process using strong one-electron oxidants.

AFOSR Program Manager: D. W. Elliott

COMPLETED PROJECT SUMMARY

1. TITLE: Resonance Spectra of Molecules Related to Laser Materials

2. PRINCIPAL INVESTIGATOR: Dr. Thomas M. Dunn
Department of Chemistry
University of Michigan
Ann Arbor, Michigan

3. INCLUSIVE DATES: 1 February 1969 - 31 January 1973

4. GRANT NO.: AFOSR 69-1715

5. COSTS AND FY SOURCE: $45,514 FY 69; $48,000 FY 71

6. SENIOR RESEARCH PERSONNEL: None

7. JUNIOR RESEARCH PERSONNEL: L. C. Cross, S. L. Gaudioso, A. H. Francis, J. H. Thirtle

8. PUBLICATIONS:

"The Electronic Excited State Spectrum of the Ruby," T. M. Dunn and A. H. Francis, Phys. Rev. Letters, 25, (No. 11) 705, (1970).

"Assignments of n-π^* Singlet States of p-Benzoquinone," T. M. Dunn and A. H. Francis, J. of Molec. Spect., in press.

"The Ground State Fundamentals of p-Benzoquinone and p-Benzoquinone d_4," T. M. Dunn and A. H. Francis, J. of Molec. Spect., in press.

"A New Absorption Band in the Spectrum of Ruby," T. M. Dunn, A. H. Francis, and J. H. Thirtle, J. of Molec. Spect., in press.

"The Excited State Spectrum of Uranyl Ion," L. C. Cross, T. M. Dunn, and J. H. Thirtle, in preparation.

"The Excited State Spectrum of Holmium in $CaWO_4$," T. M. Dunn and J. H. Thirtle, in preparation.

"The Excited State Spectrum of Inorganic Ions in EPA Glasses," T. M. Dunn, J. H. Thirtle, and S. L. Gaudioso, in preparation.

"Resonance Spectra of Molecules Related to Laser Materials," T. M. Dunn, Final Technical Report.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The detection of transitions from low lying electronically excited states to higher electronic states has been the subject of this research.

This work has required state-of-the-art optical pumping and detection equipment which was built in the workshops of the Department of Chemistry at the University of Michigan, and two apparatus and support systems are now in existence in these laboratories.

In the realm of inorganic materials, at least four excited state optical transitions have been observed and possibly two others. The detection of

such transitions is relatively trivial for organic hydrocarbons, such as naphthalene and anthracene, but difficult with organic compounds containing a carbonyl group, i.e., those having primary excited state lifetimes of the order of microseconds.

A sophisticated apparatus has been constructed capable of correlating excited state electronic absorption spectra with luminescing low lying "metastable" states having lifetimes $\gtrsim$ 50 microseconds. The techniques involved and the experience obtained in this field will be of great value in the future in an understanding of the more complex electro-optical properties of materials and have led to a situation where new detection methods (OMA) will now allow rapid exploitation of this important but difficult area of optical spectroscopy.

This development has given the capability of lifetime measurements of both emission from the lowest excited electronic state, as well as measurement of the decay lifetime of the excited electronic state absorption. It is, therefore, now possible to correlate any observed excited state absorption with the characteristics of the lowest lying electronic state and to thereby confirm the nature of electronic states involved.

As might have been obvious from this group's previous detection of excited state transitions in ruby, this has been used as a "guinea-pig" for the excited state transition lifetimes. As expected, there is a perfect correlation between the decay of the R_1, R_2 lines of the $^2E(\overline{E}$ and $2\overline{A})$ states of Cr^{3+}, and the lifetime of the excited state absorption at 666.20 nm and 667.44 nm has been confirmed.

Other materials examined in detail were:

Doped Crystals

Ho^{3+} in $CaWo_4$
Ni^{2+} in MgF_2
Nd^{3+} in CaF_2
Mn^{3+} in Spinel
Mn^{4+} in Cs_2GeF_6

Doped Glasses

$Cr(acac)_3$ in EPA*
$Co(acac)_3$ in EPA
$Mn(acac)_3$ in EPA
Uranium glass

*EPA = ethyl ether, isopentane, ethyl alcohol mixture.

Excited state absorption spectra have been definitely detected in the holmium compound, the uranium glass, and the $Cr(acac)_3$ in EPA glass, while the Ni^{2+} and Mn^{3+} compounds indicate the presence of transitions but no detectable luminescence which can be used to check the origin of the excited state transition.

The Ho^{3+} om $CaWo_4$ has revealed four relatively sharp lines at the following positions and polarizations:

(1) 352.61 nm $E \parallel$ c axis of $CaWo_4$

(2) 337.61 nm $E \perp$ c " " "

(3) 337.58 nm $E \parallel$ c " " "

(4) 336.65 nm $E \perp$ c " " "

The most interesting sample examined was that of uranyl ion in glass where there is a significant difference between the two measured lifetimes. Thus, the lifetime of the emission luminescence was found to be about 304 microseconds at $300^{o}K$ while that of the excited state absorption is about 496 microseconds under the same condition. This result holds at lower temperatures (about $100^{o}K$) and is presently being more thoroughly analyzed.

AFOSR Program Manager: D. W. Elliott

COMPLETED PROJECT SUMMARY

1. TITLE: Ultra-Fast Reaction Rates in Solution Related to Electrochemistry and Corrosion

2. PRINCIPAL INVESTIGATOR: Dr. Edward M. Eyring
Department of Chemistry
University of Utah
Salt Lake City, Utah

3. INCLUSIVE DATES: 1 January 1969 - 31 December 1972

4. GRANT NO.: AFOSR 69-1717

5. COSTS AND FY SOURCE: $72,275 FY 69; $56,702 FY 70; $54,470 FY 71
$53,646 FY 72; $18,335 FY 72

6. SENIOR RESEARCH PERSONNEL:

Dr. J. J. Auborn	Dr. J. T. Knudtson
Dr. B. C. Bennion	Dr. J. Lang
Dr. D. L. Cole	Dr. G. Macri
Dr. R. D. Farina	Dr. J. D. Owen
Dr. R. C. Graham	Dr. L. D. Rich
Dr. P. Hemmes	Dr. R. G. Sandberg
Dr. G. H. Henderson	Dr. Z. A. Schelly
Dr. J. E. C. Hutchins	Dr. P. Warrick, Jr.
Dr. J. G. Kepros	Dr. R. D. White

7. JUNIOR RESEARCH PERSONNEL:

W. Herrmann, Jr.	D. J. Lentz
L. P. Holmes	S. L. Olsen

8. PUBLICATIONS:

"Kinetics of Aqueous Scandium(III) Perchlorate Hydrolysis and Dimerization," D. L. Cole, L. D. Rich, J. D. Owen, and E. M. Eyring, Inorg. Chem., 8, 682 (1969).

"Hydrolysis Kinetics of Dilute Aqueous Chromium(III) Perchlorate," L. D. Rich, D. L. Cole, and E. M. Eyring, J. Phys. Chem., 73, 713 (1969).

"A Concentration-Jump-Relaxation Method Study of the Kinetics of the Dimerization of the Tetrasodium Salt of Aqueous Cobalt(II)-4,4',4",4"'-tetrasulfophthalocyanine," Z. A. Schelly, R. D. Farina, and E. M. Eyring, J. Phys. Chem., 74, 617 (1970).

"Kinetics of Aqueous Indium(III) Perchlorate Dimerization," E. M. Eyring and J. D. Owen, J. Phys. Chem., 74, 1825 (1970).

"Evaluation of Rate Constants Utilizing Relaxation Data Obtained at Variable Ionic Strength," Z. A. Schelly, R. D. Farina, and E. M. Eyring, Monatsh. Chem., 101, 493 (1970).

"Dimerization Kinetics of Aqueous Gallium(III) Perchlorate," J. D. Owen and E. M. Eyring, J. Inorg. Nucl. Chem., 32, 2217 (1970).

"Kinetics of the Hydrolysis of Aqueous Indium(III) and Gallium(III) Perchlorate," P. Hemmes, L. D. Rich, D. L. Cole, and E. M. Eyring, J. Phys. Chem., 74, 2859 (1970).

"Bonding in Dye Aggregates. Energetics of the Dimerization of Aqueous Cobalt(II)-4,4',4",4"'-Tetrasulfophthalocyanine Ion," Z. A. Schelly, D. J. Harward, P. Hemmes, and E. M. Eyring, J. Phys. Chem., 74, 3040 (1970).

"Effect of the Solvent on the Kinetics of Diazotization," Z. A. Schelly, J. Phys. Chem., 74, 4062 (1970).

"Kinetics of Hydrolysis of Aqueous Ferric Ion," P. Hemmes, L. D. Rich, D. L. Cole, and E. M. Eyring, J. Phys. Chem., 75, 929 (1971).

"Spectrophtometric Dissociation Field Effect Kinetics of Aqueous Acetic Acid and Bromocresol Green," J. J. Auborn, P. Warrick, Jr., and E. M. Eyring, J. Phys. Chem., 75, 2488 (1971).

"A Square Wave Dissociation Field Effect Pulse Generator for Use With Spectrophotometric Detection," S. L. Olsen, R. L. Silver, L. P. Holmes, J. J. Auborn, P. Warrick, Jr., and E. M. Eyring, Rev. Sci. Instrum., 48, 1247 (1971).

"Specific Rates in the Acid Dissociation-Ion Recombination Equilibrium of Dilute Aqueous Hydrazoic Acid at 25°," J. J. Auborn, P. Warrick, Jr., and E. M. Eyring, J. Phys. Chem., 75, 3026 (1971).

"Comproportionation Kinetics of Stable Violene Radical Ions," B. C. Bennion, J. J. Auborn, and E. M. Eyring, J. Phys. Chem., 76, 701 (1972).

"Dye Amplifiers Pumped by One- and Two-Photon Processes," J. G. Kepros and E. M. Eyring, Appl. Phys. Lett., 20, 160 (1972).

"Viscosity Effects on Ion Recombination Kinetics: Bromocresol Green in Water-Glycerol Mixtures," P. Warrick, Jr., J. J. Auborn, and E. M. Eyring, J. Phys. Chem., 76, 1184 (1972).

"The Oxidation of Sodium Salicylate by Cobalt(III) in Aqueous Perchloric Acid," R. G. Sandberg, J. J. Auborn, E. M. Eyring, and K. O. Watkins, Inorg. Chem., 11, 1952 (1972).

"Experimental Evidence of an X-Ray Laser," J. G. Kepros, E. M. Eyring, and F. W. Cagle, Jr., Proc. Nat. Acad. Sci. U.S., 69, 1744 (1972).

"Kinetics of Acid Dissociation-Ion Recombination of Aqueous Methyl Orange," R. G. Sandberg, G. H. Henderson, R. D. White, and E. M. Eyring, J. Phys. Chem., 76, 4023 (1972).

"Kinetics of Octylphenyl Polyoxyethylene Alcohol Micelle Dissociation by a Stopped Flow Technique," J. Lang, J. J. Auborn, and E. M. Eyring, J. Colloid Interface Sci., in press.

"Ultra-Fast Reaction Rates in Solution Related to Electrochemistry and Corrosion," E. M. Eyring, Final Technical Report.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

In terms of its breadth of impact, the report of evidence for an experimental x-ray laser was the most important single achievement of this four-year research effort. In essence, the approximately 20 nsec duration, 30 joule pulse of 1.06 m radiation from a Nd:glass laser incident on a glass-aqueous copper sulfate-Knox gelatin "sandwich" apparently produces a weak,

collimated pulse of "hard" x-rays. Although this phenomenon has been reproduced elsewhere, its interpretation is hotly disputed at the present time by the national laser community.

There appear to be at least four possible eventual outcomes to this research: (1) The reported effect has a trivial explanation (such as Boster's claimed triboelectric effect) and will have served merely to re-stimulate interest in attempting ingenious, inexpensive solutions to the x-ray laser puzzle rather than the incredibly expensive approaches espoused by Lax, Duguay, and others who have dominated this field. (2) The Kepros effect is nontrivial but is also not an x-ray laser in which case a new physical phenomenon may come to light. (3) The Utah laser really is a very weak, pulsed x-ray laser that after thorough elucidation will suggest the way to construct practically important "hard" x-ray lasers. (4) The Utah laser will evolve directly into a practically important "hard" x-ray laser. Unfortunately, the irreproducibility of the experimental effect does not lend itself to a rapid clarification of the question as to which of these outcomes will finally prevail. Present indications are that outcomes (1) and (4) are improbable.

A second achievement of this research program has been the refinement of the electric field jump relaxation technique in terms both of accessible time range [down to relaxation times τ as short as 20 nsec] and of detectable absorbance changes [into the ultra-violet]. Experimental evidence has been developed for protolytic reactions in aqueous solutions being non-diffusion controlled in the case of several acid-base indicators. This is not an unexpected result, but until now, theoretical speculations by Schurr and others along these lines have had comparatively little supporting experimental evidence involving such small ions. The expected more important consequence of this effort will be the feasibility of measuring rates and elucidating mechanisms of a host of carbonium ion and carbanion reactions in non-aqueous solvents that have long been the subject of conjecture on the part of physical organic chemists.

The kinetics and mechanism of dye molecule dimerization in aqueous and non-aqueous media has been a third area of significant achievement for this research program. Stopped-flow concentration jump experiments have revealed that central metal cations play an important role in the kinetics of stacking of several phthalocyanine complex ions. These dye monomers might have been expected, because of their considerable size and common electrostatic charge, to interact in a manner quite independent of the central metal ion. It remains to be seen whether these kinetic studies will have any practical ramifications for the photographic industry in which these dyes are utilized.

AFOSR Program Manager: Dr. W. L. Ruigh

COMPLETED PROJECT SUMMARY

1. TITLE: Stable Silicon Compounds of Unusual Valence Related to the Synthesis of Improved Polymers

2. PRINCIPAL INVESTIGATOR: Dr. Alan G. MacDiarmid
Department of Chemistry
University of Pennsylvania
Philadelphia, Pennsylvania

3. INCLUSIVE DATES: 1 September 1969 - 30 November 1973

4. CONTRACT NO.: AFOSR 70-1836

5. COSTS AND FY SOURCE: $16,589 FY 70; $16,589 FY 71; $16,589 FY 72; $26,637 FY 73

6. SENIOR RESEARCH PERSONNEL: Dr. M. Akhtar, Dr. A. D. Berry, Dr. S. K. Gondal, Dr. C. M. Mikulski, Dr. P. J. Russo

7. JUNIOR RESEARCH PERSONNEL: P. M. Broudy, J. Chu, D. C. Weber

8. PUBLICATIONS:

"An Even-Electron, Paramagnetic Silicon Species, $Cl_2Si(bipyridyl)_2$," P. M. Broudy, A. D. Berry, B. B. Wayland, and A. G. MacDiarmid, J. Amer. Chem. Soc., 94, 7577 (1972).

"Stable Cations Containing Silicon," A. G. MacDiarmid, Intra-Science Chem. Rept., 7, 4, 83 (1973).

"Synthesis and Properties of Dimethyl-Silicon:.m Bipyridylide," C. M. Mikulski and A. G. MacDiarmid, in preparation.

"Synthesis of a Novel, Even-Electron, Paramagnetic Silicon Compound, $Na[(CH_3)_3Si(bipyridyl)]$," P. J. Russo and A. G. MacDiarmid, in preparation.

"Synthesis and Properties of a Novel, Even-Electron, Paramagnetic Silicon Compound, $Cl_2Si(bipyridyl)_2$," A. D. Berry, J. Chu, and A. G. MacDiarmid, in preparation.

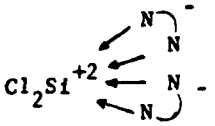
"Stable Silicon Compounds of Unusual Valence Related to the Synthesis of Improved Polymers," A. G. MacDiarmid, Final Technical Report.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

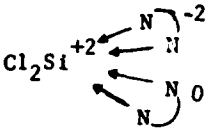
Silicones, which contain silicon in its usual +4 formal oxidation state, make up a very important class of polymers. The present research was performed in order to investigate a new type of stable silicon compounds involving 2,2'-bipyridyl, which has been reported as containing silicon in oxidation states less than four. This was done in order to ascertain whether such compounds might form the basis of a new class of silicone polymers. The most

important, previously-known stable compound of this type, the intensely green $Cl_2Si(bipy)_2$ (where bipy = 2,2'-bipyridyl), reported by Herzog et al in 1963, was stated to be constituted from dichlorosilylene, Cl_2Si, (the silicon analog of dichlorocarbene), having silicon in a +2 oxidation state coordinated to two bipyridyl molecules.

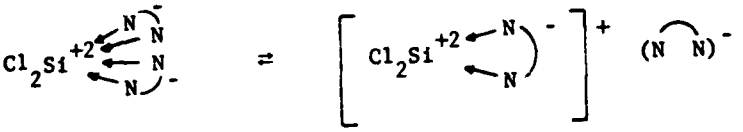
In the present research it was found that this was not the case and that the compound actually contained silicon in a +4 oxidation state. The compound was found to be a paramagnetic thermally-populated triplet molecule, even though it is an even-electron species. It may be regarded as being derived from the coordination of two bipyridyl radical anions, $(bipy)^-$, to a dichlorosiliconium cation, Cl_2Si^{+2}, viz.



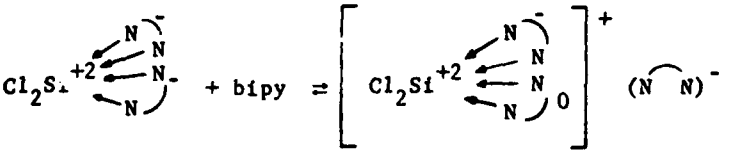
Since the most likely source of electrons on the bipyridyl radical anions is the silicon, this may be regarded as the first stable species to contain a siliconium ion. The molecule is an example of a singlet-triplet spin equilibrium species, where the diamagnetic form may be represented by the valence bond formulation



At room temperature there is an average of approximately 0.33 unpaired electrons associated with each undissociated bipyridyl molecule. In toluene solution, two different paramagnetic species are shown to be present from epr studies. It is believed that partial ionization to ion pairs occurs as follows:



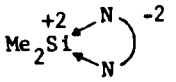
Addition of free bipyridyl to a toluene solution almost eliminates the triplet signal which is replaced by a new very strong signal which is believed to be formed by electron transfer as shown:



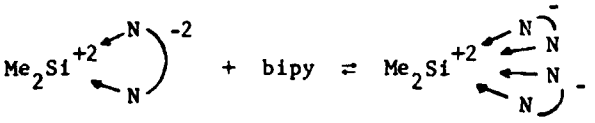
When Me_2SiCl_2 and Na_2bipy were permitted to react, a new, intense red-brown, diamagnetic compound $Me_2Si(bipy)$ was formed:

$$Me_2SiCl_2 + Na_2bipy \longrightarrow Me_2Si(bipy) + 2NaCl$$

This may be regarded as being formed by the coordination of a $(bipy)^{-2}$ ion to a Me_2Si^{+2} ion, viz.



When free bipyridyl is added to a solution of $Me_2Si(bipy)$ in toluene, it becomes strongly paramagnetic:



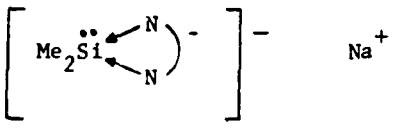
The compound again becomes diamagnetic when the bipyridyl is sublimed off. On heating, or on exposure to oxygen, bipyridyl is liberated, viz.

$$xMe_2Si(bipy) \xrightarrow{\Delta} xbipy + (Me_2Si)_x$$

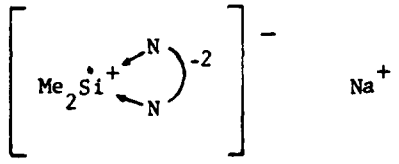
$$xMe_2Si(bipy) \xrightarrow{O_2} xbipy + (Me_2SiO)_x$$

Also formed from Me_2SiCl_2 and Na_2bipy, when excess of the latter reagent is used, is the new, intense purple compound, $[Na\ Me_2Si(bipy)]$.

This may be formulated as being derived from the coordination of a $(bipy)^-$ ion with dimethylsilylene, viz.



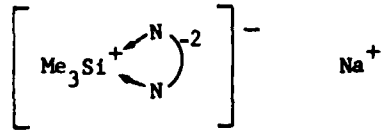
or by the coordination of a $(bipy)^{-2}$ ion with a Me_2Si ion:



The new, intense red compound, $Na[Me_3Si(bipy)]$, is formed by the reaction of Me_3SiCl with Na_2bipy, viz.

$$Me_3SiCl + Na_2bipy \longrightarrow Na[Me_3Si(bipy)] + NaCl$$

This species is most interesting, since although it is an even-electron molecule, it is also paramagnetic (0.5 unpaired electron per molecule). The exact constitution of the compound is not yet known, but it is believed that it may be regarded as being derived from the coordination of a $(bipy)^{-2}$ ion to a Me_3Si^+ ion, viz.



Since such a species would be diamagnetic, partial disproportionation must therefore occur, viz.

$$2[Me_3Si^+(bipy)^{-2}Na^+] \rightleftharpoons [Me_3Si^+(bipy)^-Na^+]^+[Me_3Si^-(bipy)^-Na^+]^-$$

This research appears to have opened up a novel area of silicon chemistry in which radical anions rather than anions or neutral molecules may act as coordinating ligands.

AFOSR Program Manager: Dr. W. L. Ruigh

COMPLETED PROJECT SUMMARY

1. TITLE: Chemistry of Photopolymer Light-Sensitive Systems Relevant to Radar and Other Displays

2. PRINCIPAL INVESTIGATOR: Dr. J. David Margerum
Exploratory Studies Department
Hughes Research Laboratories
Malibu, California

3. INCLUSIVE DATES: 1 January 1968 - 31 December 1972

4. CONTRACT NO.: F44620-68-C-0043

5. COSTS AND FY SOURCE: $45,976 FY 68; $45,993 FY 69; $40,002 FY 70; $40,526 FY 71; $40,168 FY 72

6. SENIOR RESEARCH PERSONNEL: Dr. R. G. Brault
Dr. L. J. Miller
Mr. J. B. Rust
Dr. Shi-Yin Wong

7. JUNIOR RESEARCH PERSONNEL: J. E. Jensen
A. M. Lackner
M. J. Little
H. J. Moe
C. T. Petrusis

8. PUBLICATIONS:

"Imaging by Photopolymerization," L. J. Miller, J. D. Margerum, and J. B. Rust, J. SMPTE, 77, 1177 (1968).

"The Photodecarboxylation of Nitrophenylacetate Ions," J. D. Margerum and C. T. Petrusis, J. Am. Chem. Soc., 91, 2467 (1969).

"Photopolymerization Studies: III. Thermal Sensitization and Desensitization Effects," J. B. Rust, L. J. Miller, and J. D. Margerum, Polymer Preprints, 10, 294 (1969), 157th ACS Meeting, Minneapolis, Minnesota.

"Light-Scattering Imaging by Photopolymerization," J. B. Rust, J. D. Margerum, and L. J. Miller, in Novel Imaging Systems, R. D. Murray, Ed., SPSE, Washington, D. C., April 1969, pp. 173.

"Rapid Access Photopolymerization Imaging," R. G. Brault, J. A. Jenney, J. D. Margerum, L. J. Miller, and J. B. Rust, in Applications of Photopolymers, R. J. Povinelli, Ed., SPSE, Washington, D. C., April 1970, pp. 113. (Also published in SPSE's Image Technology, 13, 3, 13 April/May 1971.)

"Studies on the Mechanism of Dye-Sensitized Photopolymerization Initiation," J. D. Margerum, A. M. Tenorio, C. T. Petrusis, and M. J. Little, Polymer Preprints, 11, 634 (1970), 160th ACS Meeting, Chicago, Illinois.

"Photopolymerization Mechanisms: I. Dye-Triplet Reactions With p-Substituted Benzenesulfinate Ions," J. D. Margerum, A. M. Lackner, M. J. Little, and C. T. Petrusis, J. Phys. Chem., 75, 3066 (1971).

"Photochromic Processes by Tautomerism," J. D. Margerum and L. J. Miller, Chapter VI in Photochromism, G. H. Brown, Ed., [Vol. III of Techniques of Chemistry, A. Weissberger, Series Ed. (John Wiley-Interscience, September 1971), pp. 557.]

"Organic Based Imaging Systems," J. D. Margerum, (State-of-the-Art Review), Symposium III on Unconventional Photographic Systems, October 1971, SPSE, Washington, D. C., pp. 54.

"Photopolymerization Mechanisms: II. Rates of Ionic Dark Addition of Benzenesulfinate Ions to Acrylic Monomers," J. D. Margerum, R. G. Brault, A. M. Lackner, and L. J. Miller, submitted to J. Phys. Chem.

"The Photochromism of Benzoate Ions With Nitrobenzyl Structures: I. Formation of Aci-Nitro Transient Intermediates," J. D. Margerum and R. G. Brault, in preparation.

"The Photochromism of Benzoate Ions With Nitrobenzyl Structures: II. Kinetics of the Fading Reactions," J. D. Margerum and R. G. Brault, in preparation.

"Reactions of Aci-Nitro Anions Produced by Photolysis of Sodium 4-Nitrophenylacetate," J. D. Margerum, in preparation.

"Photopolymerization Studies: III. Thermal Sensitization and Desensitization Effects," L. J. Miller, J. D. Margerum, J. B. Rust, R. G. Brault, and A. M. Lackner, in preparation.

"Composition and Recording Techniques for Photopolymer Holography," R. G. Brault, J. A. Jenney, A. M. Lackner, J. D. Margerum, and L. J. Miller, in preparation.

"Photopolymerization Studies: IV. Metal Acrylate Films for Holography," A. M. Lackner, L. J. Miller, J. D. Margerum, and R. G. Brault, in preparation.

"Chemistry of Photopolymer Light Sensitive Systems Relevant to Radar and Other Displays," J. D. Margerum, Final Technical Report.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objective of this work was to investigate basic chemical aspects of photopolymerization image recording systems which can be used for rapid access display or optical processing applications. Studies were made on the mechanisms for dye-sensitized polymerizations of acrylic monomers in which the images are self-developing, and on the mechanisms of thermal and photochemical image-fixing reactions. Four interrelated areas were studied: (a) the formation of aci-nitro intermediates by ultraviolet photochemical reactions, and their reactions as reducing agents to inhibit dye-sensitized polymerizations; (b) the reactivity and stability of substituted benzenesulfinic acid salts as photopolymerization catalysts; (c) the effects of monomer structure and reaction conditions on the stability, photopolymerization rate, and photopolymer image characteristics; and (d) the effects of the amorphous solid state ("dry" films) on dye-sensitized photopolymerization processes. Related Hughes research projects on the applications of rapid-access photopolymerization systems were studied and are reported in regard to projection displays and holographic recordings for optical data processing and non-destructive testing.

Two novel pnotochemical processes for the formation of aci-nitro anions were studied in detail: the photodecarboxylation of nitrophenylacetate ions, and the H-transfer photochromism of benzoate ions with nitrobenzyl structures. The effect of structure and pH was investigated on the photochemical primary processes and on the kinetics of aci-nitro fading rates. The reactivity of the aci-nitro intermediates as optically produced reducing agents was also investigated and used to inhibit photopolymerizations.

A detailed mechanism for the dye-sensitized initiation of polymerization was delineated. This showed that sulfonyl free radicals from methylene blue triplet state redox reactions with benzenesulfinate ions are efficient initiators for acrylic monomer polymerization. Triplet state rate constants were measured, and Hammett equation correlations were made with the p-substituents on benzenesulfinate ions.

The thermal (dark) reaction of benzenesulfinate ions with acrylic monomers was shown to be a Michael-type ionic addition reaction to form sulfones. The reaction rate correlation with the Hammett equation for p-substituted benzenesulfinates showed that the ionic addition reactions varied very similarly to the dye triplet redox reactions. However, the steric effects of using o- in place of p-substituents slowed down the ionic addition reaction much more than the dye-triplet photopolymer initiation step. Structural variations in the acrylic monomers changed the benzenesulfinate dark reaction rates by five orders of magnitude while the photopolymer yield varied by only a factor of ten. Long lifetime photopolymerizable solutions with high light sensitivity were obtained by appropriate choices of monomer structure, catalyst structure, and solution conditions.

The diffusion-controlled excited state reactions in glassy monomer films were sufficient to produce photopolymer from dye-sensitized reactions, although with less efficiency than in liquid solutions. Photosensitive glassy films containing barium strontium acrylate showed long-term stability with benzenesulfinate catalysts.

Rapid-access large screen projection display systems were tested for light-scattering photopolymers and for surface perturbation photopolymers based on ultraviolet fixing reactions (aci-nitro) and thermal fixing processes, respectively. Access times were 0.5 to 2 sec, with red-light imaging sensitivity of about 1 to 5 mJ/cm^2.

High resolution laser hologram recording capabilities (2000 to 2500 cycles/mm) were found for photopolymerizable solutions for wet-coated films, and for "dry" glassy films. These systems provide instantaneous holographic read-out capabilities for applications in non-destructive testing or in the optical processing of radar data.

AFOSR Program Manager: Dr. W. L. Ruigh

COMPLETED PROJECT SUMMARY

1. TITLE: Adsorption of Molecules at the Electrodes of Batteries and Fuel Cells

2. PRINCIPAL INVESTIGATOR: Dr. David M. Mohilner
Department of Chemistry
Colorado State University
Fort Collins, Colorado

3. INCLUSIVE DATES: 1 January 1968 - 30 June 1973

4. GRANT NOS.: AFOSR-68-1451; AFOSR-70-1887

6. COSTS AND FY SOURCE: $32,097 FY 68; $38,931 FY 70
$37,337 FY 71

6. SENIOR RESEARCH PERSONNEL: Dr. J. C. Kreuser, Dr. P. R. Mohilner, Dr. J. Lawrence, Dr. T. N. Solie

7. JUNIOR RESEARCH PERSONNEL: L. M. Bowman, H. Nakadomari, K. Doblhofer, G. Runbeck, S. J. Freeland

8. PUBLICATIONS:

"Double Layer Effects in the Kinetics of Heterogeneous Electron Exchange Reactions," D. M. Mohilner, J. Phys. Chem., 73, 2652 (1969).

"Electrosorption of 5-Chloro-1-Pentanol at the Mercury-Solution Interfact," K. Doblhofer and D. M. Mohilner, J. Phys. Chem., 75, 1698 (1971).

"A Computer Controlled Capillary Electrometer," J. Lawrence and D. M. Mohilner, J. Electrochem. Soc., 118, 1596 (1971).

"Thermodynamic Analysis of Electrocapillary Data," P. R. Mohilner and D. M. Mohilner, in Electrochemistry, Vol. 2 of the series, "Computers in Chemistry and Instrumentation," J. S. Matson, H. B. Mark, Jr., and H. C. MacDonald, Jr., eds., Marcel Dekker, Inc., New York, 1972, pp. 3-44.

"Effect of 2-Butanol on the Activity of Sodium Sulfate in Aqueous Solutions: Implications for Electrosorption Studies," D. M. Mohilner and H. Nakadomari, J. Phys. Chem., 77, 1594 (1973).

"Activities of Organic Compounds in Aqueous Electrolyte Solutions," D. M. Mohilner, L. M. Bowman, S. J. Freeland, and H. Nakadomari, J. Electrochem. Soc., 120, 1658 (1973).

"Electrosorption of L-α-Dipalmitoylphosphatidylcholine at the Mercury Solution Interface," G. T. Runbeck, D. M. Mohilner, and T. N. Solie, submitted to Electrochimica Acta.

"Computer Controlled Differential Capacitance Measurements," D. M. Mohilner, J. C. Kreuser, H. Nakadomari, and P. R. Mohilner, to be submitted to J. Electrochem. Soc.

"Electrosorption of 2-Butanol on Mercury from Aqueous Sodium Sulfate Solutions. 1. Thermodynamic Treatment," H. Nakadomari, D. M. Mohilner, and P. R. Mohilner, to be submitted to J. Phys. Chem.

"Electrosorption of 2-Butanol on Mercury from Aqueous Sodium Sulfate Solutions. II. Non-Thermodynamic Analysis," D. M. Mohilner, H. Nakadomari, and P. R. Mohilner, to be submitted to J. Phys. Chem.

"Implications for Electrosorption Studies of the Effect of Neutral Organic Compounds on the Ionic Activity of the Supporting Electrolyte," D. M. Mohilner and H. Nakadomari, in preparation.

"On the Importance of Activity Measurements for Experimental Electrosorption Studies of Organic Compounds," D. M. Mohilner and H. Nakadomari, in preparation.

"On the Congruence of Electrosorption Isotherms for Neutral Organic Compounds," D. M. Mohilner, in preparation.

"Interpretation of Electrosorption Isotherms for Neutral Organic Compounds in Terms of a Surface Solution of Finite Thickness," D. M. Mohilner, in preparation.

"Adsorption of Molecules at the Electrodes of Batteries and Fuel Cells," D. M. Mohilner, Final Technical Report.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The overall objective of this research has been to obtain a better understanding of the processes of adsorption of organic compounds on electrodes. This is important from a purely scientific point of view because knowledge of the behavior of adsorbed organic compounds can help greatly to elucidate the structure and interactions in the inner part of the electrical double layer which is the actual site of most important electrode reactions. From the point of view of electrochemical technology, an understanding of the electrosorption of organic compounds is vital for many diverse applications including fuel cells, batteries, electrocatalysis, and corrosion inhibition.

Although the study of organic electrosorption was started around the turn of the century with the pioneering work of Gouy, the understanding of the adsorption process progressed only slowly and was still in a highly unsatisfactory state at the time this research was begun. At that time, there were two conflicting theories of organic electrosorption, one promoted primarily by the Soviet school, the other primarily by British groups. The theoretical conflict centered around the question which electrical variable, the electrode potential, or the charge density on the electrode surface, was the "primary" electrical variable controlling electrosorption. Specifically, the question was whether electrosorption isotherms for organic compounds were "congruent" with respect to electrode potential or charge density. Congruence was expressed by assuming the validity of the following equation

$$\exp\left(-G^{o}_{ads}/RT\right)\ a_{o}^{b} = F(\Gamma_{o})$$

where G^{o}_{ads} is the standard electrochemical free energy of adsorption (taken as a function either of electrode potential or charge density),

a_o^b is the activity of the organic compound in the bulk solution, and Γ_o is the surface concentration of the adsorbed organic molecules. According to the congruence concept, if the correct electrical variable is selected, the function $F(\Gamma_o)$ will be the same for all values of that variable, i.e., all parameters in the isotherm function will be independent of the electrical state of the system. The results which have been obtained in the course of this research show that when proper experimental precautions are taken, there is no evidence of congruence with respect to either charge density or electrode potential. Moreover, on the basis of the new theory of organic electrosorption which has resulted from this research, it is shown that the concept of congruence should probably be abandoned altogether. This new theory shows that congruence would imply at constant composition in the adsorbed layer that the activity coefficients of the adsorbed organic molecules, and of the adsorbed solvent molecules, would have to be independent of the electrical state. This is highly unlikely, especially in the case of adsorption from aqueous solutions, because the extent of hydrogen bonding between the adsorbed water molecules and thus their mutual energy of interaction should vary with the electric field in the inner layer. This is so because it is the electric field which determines how strongly the molecules are oriented on the surface. The stronger the orientation, the weaker will be the hydrogen bonding and thus the higher will be the energy of intermolecular interaction.

Experimental Innovations

Digital Computer Data Analysis. When this research was started, experimental electrosorption data could be obtained either with a manual Lippmann capillary electrometer or a manual AC capacitance bridge. The Lippmann electrometer was extremely tedious to use, and analysis of the data obtained with it required differentiation which, at the time, could only be done by graphical methods which are notoriously inaccurate. Therefore, one of the first things done on this project was to develop digital computer methods for the thermodynamic analysis of electrocapillary and differential capacitance data.

An effort was made to improve the technique of measuring the interfacial tension of electrodes. It was decided not to try to improve the Lippmann electrometer because a study of the Lippmann electrometer with dilute electrolyte solutions showed that this classical instrument is subject to very serious systematic errors due to the development of a finite and potential dependent contact angle at the three phase meniscus inside the capillary. Therefore, it was decided that the Lippmann electrometer should be abandoned and a new instrument based on the measurement of interfacial tension by the maximum bubble pressure method should be tried. It also appeared that automation of an instrument based on the maximum bubble pressure principle should be much easier than would automation of a Lippmann electrometer which is based on the capillary rise principle. The final result of this work was the development of the first fully automatic capillary electrometer. The new instrument is controlled by a minicomputer. It completely overcomes the disadvantages of the Lippmann electrometer. It is not at all difficult or tedious to use, and for study of the electrosorption of organic compounds, it is far superior to differential capacitance measurements. In fact, it can be said that the computer controlled capillary electrometer has reversed the instrumental preference for double layer studies.

Experiments were carried out in this laboratory to test whether, in the case of 2-butanol in aqueous sodium sulfate solutions, there was any effect on the chemical potential of the salt by the organic compound. The emf method

of measuring electrolyte activities was used, and in these experiments, a sodium ion specific electrode was employed. The results of this research showed that the organic compound exerts a great effect of the salt chemical potential. This effect was correlated with the structure making properties of the organic compound in water. It is believed that this effect is quite general. This research makes it clear that most previous organic electrosorption studies may involve very serious errors through neglect of the effect of the organic compound on the chemical potential of the electrolyte. Studies such as this one must in the future be the necessary first step before the actual electrosorption measurements are begun, because this type study provides the recipe for preparation of the series of solutions which should be used in the electrosorption measurements.

A new experimental method was developed for measurement of the activities of organic compounds in aqueous electrolyte solutions. This new method is a gas chromatographic one employing a gas chromatograph equipped with a flame ionization detector and a gas sampling valve.

The new method is capable of measuring the activities of organic compounds in aqueous electrolyte solution with an accuracy of about 0.5 per cent.

AFOSR Program Manager: D. W. Elliott

COMPLETED PROJECT SUMMARY

1. TITLE: Fundamental Studies of Electrochemical Processes

2. PRINCIPAL INVESTIGATOR: Dr. R. W. Murray and
Dr. C. N. Reilley
Department of Chemistry
University of North Carolina
Chapel Hill, North Carolina

3. INCLUSIVE DATES: 1 October 1968 - 28 February 1973

4. GRANT NO.: AFOSR-69-1625

5. COSTS AND FY SOURCE: $52,363 FY 69; $54,078 FY 70
$54,604 FY 71; $59,315 FY 72

6. SENIOR RESEARCH PERSONNEL:

Dr. J. N. Burnett	Dr. T. H. Ridgway
Dr. H. Herman	Dr. T. D. Walsh
Dr. M. Petek	Dr. W. S. Woodward
Dr. R. C. Reed	

7. JUNIOR RESEARCH PERSONNEL:

A. J. Bentz	P. Ogburn
M. A. Bradley	G. B. Park
J. R. Cockrell, Jr.	F. A. Pennington, Jr.
C. M. Elliott	R. L. Scott
L. E. Fox	W. D. Snider
P. T. Holt	P. Surana
W. W. Howland	H. L. Surprenant
J. P. Koontz	R. P. Van Duyne
J. W. Lodge	R. M. Wightman
R. L. McNeely	D. C. Young
T. E. Neal	

8. PUBLICATIONS:

"An Inexpensive Current-Voltage Booster for Electrochemical Instrumentation," W. S. Woodward, T. H. Ridgway, and C. N. Reilley, Anal. Chem., 45, 435 (1973).

"Comparative Spectroelectrochemical, Stopped-Flow Kinetic, and Polarographic Study of the Titanium (III)-Hydroxylamine Reaction," M. Petek, T. E. Neal, R. L. McNeely, and R. W. Murray, Anal. Chem., 45, 32 (1973).

"Low-Temperature Electrochemistry: I. Characteristics of Electrode Reactions in the Absence of Coupled Chemical Kinetics," R. P. Van Duyne and C. N. Reilley, Anal. Chem., 44, 142 (1972).

"Deuterium Labeling by Electrochemical Reactions," J. R. Cockrell, Jr., and R. W. Murray, J. Electrochem. Soc., 119, 849 (1972).

"Chronoamperometry, Chronocoulometry, and Chronopotentiometry," a chapter from Weissberger: Chemistry, Vol. 1, Part IIA, Wiley & Sons, N. Y., 1971, R. W. Murray.

"Low-Temperature Electrochemistry: II. Evaluation of Rate Constants and Activation Parameters for Homogeneous Chemical Reactions Coupled to Charge Transfer," R. P. Van Duyne and C. N. Reilley, Anal. Chem., 44, 153 (1972).

"Low-Temperature Electrochemistry: III. Application to the Study of Radical Ion Decay Mechanisms," R. P. Van Duyne and C. N. Reilley, Anal. Chem., 44, 158 (1972).

"Double Potential Step Chronocoulometry: Part I. A Re-examination of EC Kinetic Theory Including the Effects of Electrode Reactant and Product Adsorption," T. H. Ridgway, R. P. Van Duyne, and C. N. Reilley, J. Electroanal. Chem., 34, 267 (1972).

"Double Potential Step Chronocoulometry: Part II. Measurement of the Chemical Reaction Rate in an EC Mechanism When Both Electrode Reactant and Product Are Adsorbed," R. P. Van Duyne, T. H. Ridgway, and C. N. Reilley, J. Electroanal. Chem., 34, 283 (1972).

"Spectroelectrochemistry--Application of Optically Transparent Minigrid Electrodes Under Semi-Infinite Diffusion Conditions," M. Petek, T. E. Neal, and R. W. Murray, Anal. Chem., 43, 1069 (1971).

"Electrochemical Studies of Thioxanthene, Thioxanthone, and Related Species in Non-Aqueous Media," P. T. Kissinger, P. T. Holt, and C. N. Reilley, J. Electroanal. Chem., 33, 1 (1971).

"Specular Reflectance in Thin-Layer Electrochemistry," P. T. Kissinger and C. N. Reilley, Anal. Chem., 42, 12 (1970).

"Autocatalysis of the Kinetic Wave of Acetylacetone in Acetonitrile Solvent," T. E. Neal and R. W. Murray, Anal. Chem., 42, 1654 (1970).

"Two-Dimensional Crystals in Adsorption of Lead Halides," R. L. McNeely, P. Surana, H. Herman, and R. W. Murray, submitted to Anal. Chem.

"Edge Diffusion and Resistance in Thin Layer Electrochemistry," J. N. Burnett, W. R. Heineman, G. B. Park, and R. W. Murray, in preparation.

"Anodic Non-Aqueous Electrode Reactions of Organic Anions," T. E. Neal and R. W. Murray, submitted to Anal. Chem.

"Spectroelectrochemical Measurements of Chemical Reaction Rates," R. P. Van Duyne, T. H. Ridgway, and C. N. Reilley, in preparation.

"Device for Automatic Compensation of Systematic Errors in Chronocoulometry," W. S. Woodward, T. H. Ridgway, and C. N. Reilley, in preparation.

"A Double Potential Step Investigation of Oxidation of 9, 10-Diphenylanthracene in the Presence of 4-Cyanopyridine," T. H. Ridgway and C. N. Reilley, in preparation.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

This project has had as its main theme study, on a broad front of research, the modes of energy transfer which can accompany an electrochemically-induced charge transfer process. A variety of high energy, reactive radicals have been studied, including radical anions and cations, and neutral radicals, and a framework of decay pathways and strategy for experimental investigations has been proposed. Significant aspects of electrochemical techniques, theory, and instrumentation developed during these studies of energy transfer modes have been (1) development of cryoelectrochemistry, (2) continued improvement of spectroelectrochemical methods, (3) introduction of stopped-flow kinetic methods as applied to electrochemically important chemical reactions, and (4) treatments of the cases of reactant and product adsorption in studies of electrochemically-induced decay reactions.

This project has also discovered an instance of surface solubility-controlled two-dimensional crystal formation in adsorption of a metal complex on a mercury electrode from aqueous solution.

In the low-temperature electrochemistry, while the sub-ambient temperatures have been used occasionally to facilitate electrochemical detection of reactive intermediates, the use of cryoelectrochemistry has not been placed on a practical footing with modern electrochemical techniques.

The use of optically transparent electrodes (OTE) and ultraviolet and visible spectroscopic approaches to follow the courses of electrochemical reactions has been an important area of development to which this laboratory made a sizable contribution. The merit of fast double potential step (DPS) experiments have proven substantial in detection and quantitative kinetic study of unstable electrogenerated species.

This group introduced the essential, simple ideas and rationale for application of stopped flow (S-F) kinetic spectrometry to the kinetics and mechanisms of chemical reactions which were proposed on potential sub-components of electrochemical reactions, and have continued this theme on S-F kinetic investigations of radical anion protonation.

In the course of developing kinetic data on the quinone radicals, they have also greatly improved several aspects of the S-F kinetic spectrometer system. In one phase of the research, the S-F system was subjected to computerized data acquisition with extensive software capability for data reduction. In a second phase, they have incorporated a Harrick rapid scanning monochromator for measurement of solution spectra in 2 millisecond intervals during the kinetic decay. It is believed that this system, when completed, will represent a new level of state-of-the-art in S-F kinetic spectrometry instrumentation.

This group has developed several electronic devices as aids to electrochemical experiments. One of these was a device for the automatic compensation of systematic errors in chronocoulometry and related techniques. This technique was published in Analytical Chemistry.

Another application of electrochemistry to the preparation of a high purity, specifically deuterium-labeled aromatic compound, was published in the Journal of the Electrochemical Society.

As part of a long-standing interest in surface chemistry of electrochemical adsorptions, this laboratory has conducted a re-investigation of lead

halide adsorptions which produces a picture of two-dimensional crystallization events. This group also participated heavily in the development of the thin-layer electrochemical method, and have carried out a study of edge diffusion and resistance effects using a spectroelectrochemical approach.

Edge diffusion in a thin layer electrochemical cell refers to lateral mass transport of cell reactant from solution volume outside the perimeter of the working electrode. Its consequence is a charge-time "drift" in thin layer potential step charge-time curves and impairment of the accuracy of coulometric measurements. Elimination of this drift effect is possible with "getter" electrodes around the working electrode perimeter, but this approach is not always feasible or advantageous, and a better quantitative understanding of the edge diffusion process would be useful. A theory has been proposed and experiments performed. The general features of the theory have been confirmed, and several conclusions have been reached.

AFOSR Program Manager: Mr. D. W. Elliott

COMPLETED PROJECT SUMMARY

1. TITLE: The Effect of Wave Length on the Degradation of Certain Polymers

2. PRINCIPAL INVESTIGATOR: Dr. W. Albert Noyes, Jr.
Department of Chemistry
University of Texas
Austin, Texas

3. INCLUSIVE DATES: 15 January 1971 - 15 June 1973

4. GRANT NO.: AFOSR-71-3031

5. COSTS AND FY SOURCE: $15,262 FY 71; $15,262 FY 72

6. SENIOR RESEARCH PERSONNEL: Dr. T. L. Brewer
Dr. R. A. Gorse
Dr. S. H. Jones

7. JUNIOR RESEARCH PERSONNEL: None

8. PUBLICATIONS:

"Photophysical Processes of m-Difluorobenzene," T. L. Brewer, J. Phys. Chem., 75, 9, 1233 (1971).

"The Effect of Wave Length on the Degradation of Certain Polymers," W. A. Noyes, Jr., T. Brewer, S. H. Jones, and R. A. Gorse, Final Technical Report.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objective of this work was to find some of the steps which lead to polymer degradation in the hope that with more complete information, some of the pitfalls may be avoided. Polymeric substances form an important part of modern life. They have properties which vary greatly in hardness, in ductility, and in elasticity. The many uses to which they are put in paints, in cosmetics, in clothing, and in building materials require that they be exposed to sunlight or to artificial light. One might almost say that sensitivity to visible or ultra-violet light is a universal characteristic of plastic materials. Often this sensitivity is so great as to render certain materials virtually useless. One of the great needs of the plastic and synthetic fiber industry is to avoid this susceptibility to radiation. Certain classes of compounds, aldehydes, ketones, and esters are particularly amenable to plastic formation. Many of them are extremely light sensitive, and certain types of plastics are to be avoided if light stability is desired. Polymers made of these compounds when exposed to light decompose in two important ways. One leads to very rapid disintegration and is relatively hard to avoid. The other leads only to a gradual change in properties, generally so slow that utility of the plastic may not be seriously impaired for some time.

Research under this grant has been largely on the following compounds: polycaprolactone, polyvinylacetate, polyacrylic acid, and polydiallylphthalate.

This paper will only cite the work on the photolysis of polydiallylphthalate. (PDAP).

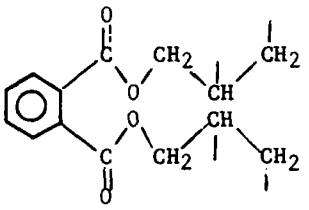
The goal of this project was to study the photodegradation of a polymer system containing more than one chromophoric group. If the different chromophores absorb at different wavelengths, the study of the wavelength effect on the degree and mode of photodegradation should yield information on the mechanism and rate of energy relaxation through the polymer chain.

At the instant of absorption the photon energy is localized in the particular vibronic mode of the chromophore responsible for adsorption. If that energy is not rapidly released via bond scission or isomerization, the energy may become delocalized through the molecule. This delocalization, such as through vibrational-electronic coupling, may result in bond breakage at some point physically removed from the point of the initial excitation. If bonds are broken in the backbone of the polymer chain, there will be a resultant change in the number average molecular weight of the polymer. Molecular elimination would cause only a slight change in molecular weight but should give rise to detectable quantities of reaction products.

Experimental

The polymeric material selected for study was polydiallylphthalate (PDAP). The sample was obtained as a viscous, clear, colorless liquid from the City Chemical Company of New York. It had a density of 1.096 grams cm^{-3} and a viscosity of 11.2 cp at 28°C. (Water has a viscosity of 0.82 cp at 28°C.)

The structure of the monomer unit is:



$M_{monomer}$ = 246 gms $mole^{-1}$

PDAP is a polydiester which can exist in the dimeric or trimeric form as well as high molecular weight chains (M = 10^4 - 10^5 gms $mole^{-1}$) with large numbers of monomer units. It has found industrial utility in resins and adhesives, coatings, laminates, as a molding material, as well as in producing fire resistant products. The high degree of photostability found in the present study suggests that PDAP could also be put to good use as an extremely efficient UV filter, particularly in extra-terrestrial situations.

The intrinsic viscosity of the PDAP was determined in benzene solutions and in n-heptane solutions.

The intrinsic viscosity of a macromolecule is a measure of the volume the macromolecule occupies per unit mass of polymer in an infinitely dilute solution. The intrinsic viscosity of PDAP was determined to be 1.75 cm^3 gm^{-1} in benzene at 28°C. and 0.65 cm^3 gm^{-1} in heptane at 28°C. These results indicate that benzene is a "good" solvent for PDAP and that heptane is a "poor" solvent. The same conclusions would be drawn from the comparative solubilities of the PDAP in the two solvents. Thus, in benzene, the polymer expands due to solvent-solute affinity whereas in heptane there is a contraction due to solvent-solute repulsions and, in fact, the PDAP occupies about 1/3 the volume per unit mass in heptane that it does in benzene.

PDAP is a very strong absorber of ultra-violet light, and it was thus necessary to use extremely dilute solutions to obtain absorption spectra on a Cary 14 Spectrometer in a 1 cm absorption cell. Spectra were obtained in n-heptane and in water.

Irradiation with UV light with wavelengths corresponding to the different transitions allows one to concentrate excitation energy initially in a particular location in the polymer molecule. The observation of bond scission at a point removed from the original site of excitation furnishes information on the efficiency and mode of internal energy relaxation processes.

Irradiation of PDAP was performed under various experimental conditions of incident wavelength and bandpass UV light, on the neat liquid or in benzene solution, and in the presence or absence of atmospheric oxygen. The different conditions employed are summarized in Table I.

TABLE I

Run #	Solvent	Pressure Torr	Lamp	Wavelength nm	Bandpass nm	Time hrs
1	None	2×10^{-8}	Hg-Xe	302	1.6	6
2	None	2×10^{-8}	Hg-Xe	280	2.5	6
3	None	Atm	Hg-Xe	280	2.5	24
4	Benzene 2:1	Atm	Hg-Xe	280	2.5	30
5	Benzene 2:1	4×10^{-7}	Hg-Xe	>236	(7-54 Filter)	8
6	Benzene 2:1	1×10^{-6}	Xe	225	2.5	24
7	None	Atm	Xe	233	5.0	12
8	None	Atm	Xe	>190	>Full Beam	17
9	None	Atm	Xe	>190	>Full Beam	56

Discussion

Absorption by aromatic compounds within the phenyl chromophore seldom results in ring opening. The frequently encountered processes are those of isomerization of the substituent positions on the phenyl ring, and intermolecular energy transfer to the substituents with subsequent bond scissions or rearrangements external to the phenyl ring. Isomerization could occur via intermediates with the benzvalene, fulvene, or prismane structures. Light absorption by the ester chromophore may result in either or both of the Norrish Type I and Type II processes for carbonyl group decompositions. The Type I process results in radical formation via bond scission within or adjacent to the carbonyl group. Secondary decomposition of the radical species often gives CO and/or CO_2 as major products. The Type II process is a concerted reaction resulting in the formation of two stable molecules, in this case, a substituted benzoic acid and the re-formation of an allyl end-group. Both of these processes should result in a degradation of the polymer chain and an observable decrease in the number average molecular weight of PDAP. The failure to observe any change in the intrinsic viscosity of

the PDAP samples implies that none of these processes are operative in PDAP upon absorption of UV light.

In summary, the PDAP sample investigated appears to be remarkably inert to UV light at least on the time scale employed here. The fact that all the light below 310 nm is absorbed and that there is no emission, as well as no observable chemical change, indicates that PDAP is extremely efficient in relaxation of vibronic excitation energy into vibrational modes of the polymer structure. The results indicate that there are no "energy sinks" or "weakest links" capable of collecting the vibrational energy to cause bond scission prior to thermal energy release to the surroundings.

The possibility of using PDAP as a UV filter, particularly in extra-terrestrial situations, is suggested by its photostability, large absorption coefficients below 310 nm, and its transparency to light above 310 nm.

AFOSR Program Manager: D. W. Elliott

COMPLETED PROJECT SUMMARY

1. TITLE: High Resolution Gas Phase Infrared Absorption Spectra of Simple Gases

2. PRINCIPAL INVESTIGATOR: Dr. John Overend
Department of Chemistry
University of Minnesota
Minneapolis, Minnesota

3. INCLUSIVE DATES: 1 December 1970 to 30 November 1972

4. GRANT NO.: AF-AFOSR-71-2014

5. COSTS AND FY SOURCE: $9,834 FY 71; $12,814 FY 72

6. SENIOR RESEARCH PERSONNEL: Dr. T. Nakagawa

7. JUNIOR RESEARCH PERSONNEL:

K. Davis	R. Lin
J. Giguere	S. Vincent
A. C. Jeanotte	V. Wang

8. PUBLICATIONS:

"Infrared Spectra of CD_3I Isolated in an Argon Matrix," J. Overend and D. R. Anderson, Spectrochim. Acta 28A, 1225 (1972).

"Matrix Infrared Spectra and Anharmonic Force Field of NCO^-," J. Overend, D. F. Smith, Jr., J. C. Decius, and D. J. Gordon, J. Chem. Phys., in press.

"Infrared Spectra of Simple Molecules in Liquid-Argon Solution. I. CF_4," J. Overend, A. C. Jeanotte, II, and D. Legler, Spectrochim. Acta, submitted for publication.

"High Resolution Spectra of OCS Between 2000-400 cm^{-1}," J. Overend, K. A. Davis, and T. Nakagawa, to be published.

"Computer-Assisted Assignment of Vibration-Rotation Spectra," T. Nakagawa and J. Overend, to be published.

"High Resolution Gas Phase Infrared Absorption Spectra of Simple Gases," J. Overend, Final Technical Report.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The developments of particular significance are the extension of state-of-the-art experimental techniques in high-resolution spectroscopy to the mid-infrared region 2000-400 cm^{-1}. The development of techniques for the assignment and analysis of complicated rotation-vibration spectra, and the satisfactory assignment of a large number of bands of simple molecules. A great deal remains to be done, but the techniques which have been developed have been taken up by other laboratories. Work similar to that which has been pursued under this grant is now being carried out in Japan, Canada, Belgium, and Czechoslovakia, as well as in a number of other laboratories in the United States.

The results of the analysis of high resolution spectra are quite generally useful. From them, values are obtained of the molecular geometry, of the harmonic and anharmonic potential energy constants, and other quantities of primary physical-chemical importance.

One currently important use of the data is the determination of spectral assignments and appropriate analytical wavelengths for the determination of trace contaminants in gases. Some of the molecules are present as air pollutants, and the same spectra which have been investigated from a fundamental viewpoint are currently being used to measure concentration in long absorbing paths. It now appears that the tunable laser will be used widely for monitoring air pollutants, and the high resolution studies will become increasingly important as support for analytical determinations in the field. It is most satisfying that this laboratory has been instrumental in developing the basic spectroscopic techniques.

The principal interest in the data obtained in this research is in the calculation of anharmonic potential energy functions. It has been carried through a number of calculations, but this work cannot yet be claimed to be in final form. As new data are obtained, it should be possible to refine the models u' :d and ultimately acquire a fairly detailed understanding of the internal forces within molecules. Since it is these forces which hold the atoms together and which control, ultimately, all chemical processes, the understanding of these forces in some simple molecules is fairly basic to an understanding of chemistry. This particular phase of the program draws on a large body of experimental data, some of it measured in this laboratory, much of it in others, and the experimental data are acquired fairly slowly. However, most of th' computer techniques are developed, the new data will be followed as it appears, and calculations will be extended where it seems that there is useful new information to be won.

AFOSR Program Manager: D. W. Elliott

COMPLETED PROJECT SUMMARY

1. TITLE: New High Temperature Fluorocarbons--Their Preparation and Properties

2. PRINCIPAL INVESTIGATOR: Dr. Joseph D. Park
Department of Chemistry
University of Colorado
Boulder, Colorado

3. INCLUSIVE DATES: 1 December 1968 - 30 November 1972

4. GRANT NO.: AFOSR 69-1679

5. COSTS AND FY SOURCE: $63,260 FY 69; $17,270 FY 71; $24,720 FY 72

6. SENIOR RESEARCH PERSONNEL: Dr. Sea-wha Oh
Dr. Robert L. Soulen

7. JUNIOR RESEARCH PERSONNEL:

J. S. Bratholdt	G. G. Pearson
Kwan Soo Han	M. O. Riley
J. H. Newman	A. Wu

8. PUBLICATIONS:

"The Synthesis of a 1,4-Dithiocin," M. O. Riley and J. D. Park, Tetrahedron Letters, 1871 (1971).

"Vinylic Halogen Exchange Reactions in 1,2-Dihaloperfluorocycloalkenes," R. L. Soulen, B. T. Nakata, and J. D. Park, J. Fluorine Chem., 1, 235 (1971).

"Free-Radical Reactions of Silanes with 1,2-Dihalopolyfluorocycloalkenes," J. D. Park and G. G. Pearson, J. Fluorine Chem., 1, 277 (1972).

"Reactions of Aluminum Chloride with Fluorocycloalkenes with Trivalent Phosphorus," J. D. Park and G. G. I. Moore, J. Korean Chem. Soc., 17, 31 (1973).

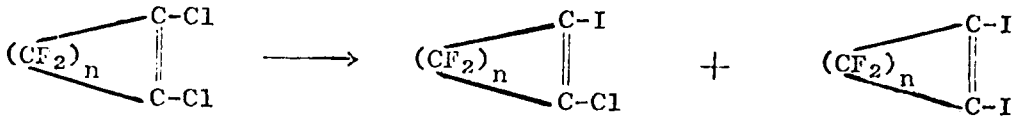
"Methanolysis of 2-Chloroformyltetrafluorocyclobutene," R. L. Soulen and J. D. Park, J. Fluorine Chem., 2, 443 (1972/73).

"New High Temperature Fluorocarbons--Their Preparation and Properties," J. D. Park, Final Technical Report.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The following objectives were carried out successfully under this grant:

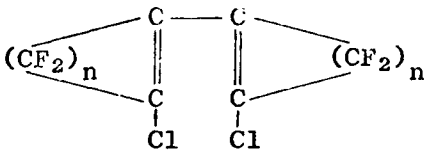
a. Great improvements in yields in the conversion of 1,2-dichloroperfluorocycloalkenes to the corresponding monoiodo- and diiodoperfluorocycloalkenes as shown below:



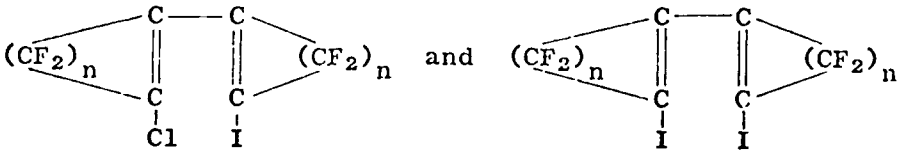
(1) (2)

n = 2, 3, and 4

b. The above compounds (1) were subjected to reductive coupling with copper and a trace amount of dimethylformamide to attain improved yields of the corresponding 2,2'-dichloroperfluoro-(bi-1-cycloalkenyl-1-yl) derivatives of the following general formula:



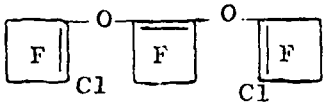
The above compounds were then converted to the corresponding mono-iodo and diiodoperfluorocycloalkenes listed below:



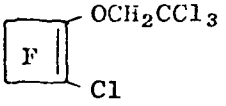
(3) (4)

Compounds (1) were then reacted with ethyleneimine, nitrogen containing heterocyclics, amines, diamines, $P(O\emptyset)_3$, and $P(OCH_3)_3$.

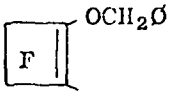
Various miscellaneous reactions were studied in attempts to prepare oxygenated derivatives of the perhalocycloalkenes in attempts to prepare compounds of the following nature:



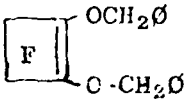
(unsuccessful)



(successful)

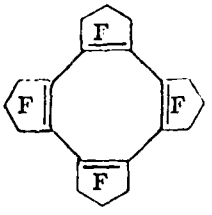


(successful)



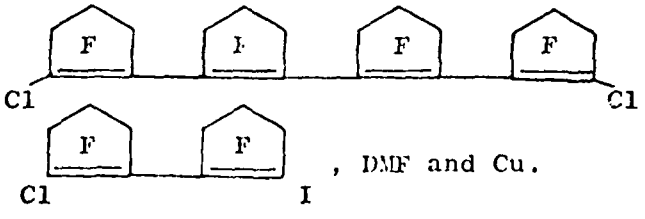
(successful)

One of the successful acomplishments in this project was proving with certainty the structure of



This compound was obtained by heating  with a trace amount of dimethylformamide in the presence of copper.

The following compound was also synthesized:

(A)  m.p. 89°

from 2 , DMF and Cu.

By conversion of one of the chlorine atoms to an iodine atom, one can envision the stepwise building up of (A) to

which should have very high thermal stability. Many of the new compounds prepared in this project should be useful intermediates as new high-temperature fluorocarbons.

AFOSR Program Manager: Dr. A. J. Matuszko

COMPLETED PROJECT SUMMARY

1. TITLE: The Effect of Atomic Interactions on the Structure and Physical Properties of Fluids

2. PRINCIPAL INVESTIGATOR: Dr. C. J. Pings
Division of Chemistry and
Chemical Engineering
California Institute of Technology
Pasadena, California

3. INCLUSIVE DATES: 1 September 1967 - 31 August 1972

4. GRANT NO.: AFOSR-68-1382

5. COSTS AND FY SOURCE: $118,926 FY 68; $123,710 FY 69; $95,000 FY 70; $75,000 FY 71; $49,900 FY 72

6. SENIOR RESEARCH PERSONNEL:

Dr. A. F. Collings	Mr. H. H. Reamer
Dr. A. F. G. Cope	Dr. R. L. Schmidt
Dr. J. G. Curro	Dr. G. D. Wignall
Dr. E. H. Henninger	

7. JUNIOR RESEARCH PERSONNEL:

R. Brown	D. L. Lau
J. G. Curro	P. F. Morrison
Erdogan Gulari	W. E. Munsil
Esin Gulari	M. A. Piliavin
V. P. Gutschick	P. K. Salzman
N. L. Helgeson	S. C. Smelser
J. F. Karnicky	H. J. Strumpf
A. Koffman	D. A. Wood
A. H. Larson	S. Y. Wu

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"Reduced State Correlations for the Self-Diffusivity of Dense Fluids," A. F. Collings, accepted by AIChE J.

"The Effect of Atomic Interactions on the Structure and Physical Properties of Fluids," C. J. Pings, Final Technical Report.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Described is progress during a five-year interval for a program of experimental and theoretical studies of forces and configurations at the molecular level in simple fluids. The general program was supported by a sequence of grants and contracts with the Directorate of Chemical Sciences of AFOSR since 1957.

Mapping of the structure of liquid argon has continued, with the completion of experiments and data analysis at twelve new thermodynamic states in the dense liquid domain. These additional experiments confirm earlier conclusions regarding systematic failure of several current integral equation theories of the liquid state. An experiment continues on the scattering of x-rays from dense argon gas, with the purpose of determining the two-body and three-body intermolecular forces.

A cryostat constructed several years ago for the purpose of measuring refractive index of confined fluids in order to explore dielectric theories of non-polar liquids has been used in the last five years for the optical measurement of density. This has permitted a concerted experimental attack on thermodynamic singularities in the critical region of argon and krypton, and has permitted quantitative characterization of anomalies in the PVT surface as the critical state is approached for those two substances. In another critical state experiment, a calorimeter was constructed for the explicit purpose of determining the nature of the heat capacity singularity near a binary consolute point. Measurements were carried out in the CH_4-CHF_3 system, in the vicinity of 130°K. For the first time for this class of systems, direct experimental verification was obtained for a λ-like divergence in the isobaric hear capacity. Singularities in transport properties near critical states have also been studied. In one instance, this involved a direct determination of the viscosity of xenon, and separately of ethane, near critical states, revealing anomalous excesses of as much as 30%, but at this point not suggesting a divergence of the type found previously for thermal conductivity.

New techniques in inelastic light scattering have been developed for study of dynamical processes in liquids. A laser light scattering apparatus was used for an extensive experimental study of dynamical correlations near the consolute point of the 2,6-lutidine water system, providing a quantitative substantiation of most of the features of the mode-mode coupling theories. The apparatus and associated data analysis techniques have now been applied to measurements of binary diffusion coefficient and thermal conductivities of conventional fluids.

AFOSR Program Manager: Dr. D. L. Ball

COMPLETED PROJECT SUMMARY

1. TITLE: The Structure of Materials and Their Interaction With Radiation

2. PRINCIPAL INVESTIGATOR: Dr. Stuart A. Rice
The James Franck Institute
University of Chicago
Chicago, Illinois

3. INCLUSIVE DATES: 1 November 1968 - 31 August 1972

4. GRANT AND CONTRACT NOS.: AFOSR-69-1663
F44620-72-C-0003

5. COSTS AND FY SOURCE: $195,884 FY 69; $172,590 FY 70
$152,741 FY 71; $160,949 FY 72

6. SENIOR RESEARCH PERSONNEL:

Dr. M. H. Cohen	Dr. J. J. Kozak
Dr. S. Fischer	Dr. Y. T. Lee
Dr. K. Freed	Dr. L. Meyer
Dr. R. Gavin, Jr.	Dr. G. C. Morris
Dr. R. Hawkins	Dr. S. Nordholm
Dr. J. Jortner	Dr. D. S. Olander
Dr. B. Katz	Dr. B. Raz
Dr. K. Kay	Dr. B. Sharf
Dr. N. R. Kestner	Dr. P. E. Siska

7. JUNIOR RESEARCH PERSONNEL:

A. S. Abramson	M. Martin
E. Achter	A. Nazarea
A. Bloch	H. Nelson
J. Boiani	S. Newman
B. Clarke	J. M. Parson
K. Evans	J. L. Richards
D. Florida	S. Risemberg
W. Gelbart	T. P. Schafer
W. Greer	R. Scheps
D. Guidotti	K. Shobotake
C. Gutman	B. Siskind
D. F. Heller	K. Spears
A. Hinds	F. P. Tully
N. Holzwarth	C. C. Venkatesh
M. H. Hui	J. Weeks
J. A. Jahnke	B. Weisman
I. Katz	J. T. Wenzel
A. Kaufman	O. Weres
H. Lemberg	H. Wilson
B. C. Lu	Y. C. Wong
A. E. Martin	

8. PUBLICATIONS:

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"Zero-Field Mobility of an Excess Electron in Fluid Argon," J. A. Jahnke, L. Meyer, and S. A. Rice, Phys. Rev., 3, 2, 734 (1971).

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"Elementary Electronic Excitations in Insulating Liquids," J. Jortner and N. R. Kestner, Proc. of the 2nd Weyl Conf., in press.

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"Energy of the Quasi-Free Electron State in Liquid and Solid Rare Gases," J. Jortner and B. Raz, Chem. Phys. Letters, in press.

"On Observing "New" States in Small Molecules," W. M. Gelbart and J. Jortner, submitted to J. Chem. Phys.

"Electronic Relaxation Processes in Large Molecules," J. Jortner, Plenary Lecture, XII IUPAC Conference, in press.

"A Comment on the V Excited State of the Ethylene Molecule," E. Miron, B. Raz, and J. Jortner, submitted to Chem. Phys. Letters.

"On the Electronic Structure of Dilute Liquid Metals: Some Properties of the Infinitely Dilute Metal/Molten Salt Mixture," I. Katz and S. A. Rice, submitted to J. Chem. Phys.

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"The Structure of Materials and Their Interaction With Radiation," S. A. Rice, Final Technical Report.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The theme of this research was to construct experimental and theoretical studies of the interrelation between electronic structure, molecular structure, and molecular motion. Phenomena dependent on these interrelations are reflected in material properties as diverse as the conductivity of liquid metals, photochemistry, phase transitions, etc. This research has attempted to isolate important features of the observations, to analyze them, to construct models which permit deeper understanding, and to test theory with experiment. The record is contained in the literature references. The categories of the effort may be given as the following:

(a) transport of matter and energy,

(b) electronic structure of disordered systems,

(c) photochemistry,

(d) electronic structure of molecular crystals,

(e) theory of liquids and phase transitions,

(f) chemical control mechanisms,

(g) general physical chemistry (especially reaction kinetics).

AFOSR Program Manager: Dr. D. L. Ball

COMPLETED PROJECT SUMMARY

1. TITLE: Atomic and Molecular Collision Dynamics in Very High Energy Chemical Systems

2. PRINCIPAL INVESTIGATOR: Dr. John W. Root
Department of Chemistry
University of California
Davis, California

3. INCLUSIVE DATES: 1 January 1968 - 30 September 1972

4. GRANT NO.: AFOSR-68-1493

5. COSTS AND FY SOURCE: $34,985 FY 68; $39,278 FY 70
$45,874 FY 71; $44,558 FY 72

6. SENIOR RESEARCH PERSONNEL: Dr. J. E. Kaizer, Dr. M. Newton, Dr. C. F. McKnight, Dr. C. Tsao, Dr. J. T. Muckerman

7. JUNIOR RESEARCH PERSONNEL: B. Lan, L. L. Lucas, F. A. Little, G. W. Mutch

8. PUBLICATIONS:

"A New Primary Process in the Ultraviolet Photolysis of CH_3I. The Direct Photolysis to :CHI," C. W. Tsao and J. W. Root, J. Phys. Chem., 76, 308 (1972).

"Reactions of Hot Methyl Radicals With H_2," C. W. Tsao and J. W. Root, submitted for publication.

"Reactions of Hot Methyl Radicals With CH and CD_4," C. W. Tsao, B. Lan, and J. W. Root, in preparation.

"Chemically Activated $^{14}CH_3CF_3$ via $^{14}CH_3+CF_3$ Recombination. I. Protective Scavenging to Eliminate CF_3 Attack on $^{14}CH_2 = CF_2$ Unimolecular Decomposition Product," G. W. Mutch and J. W. Root, in preparation.

"Chemically Activated $^{14}CH_3CF_3$ via $^{14}CH_3+CF_3$ Recombination. II. Energy Transfer With Fluorethanes," G. W. Mutch and J. W. Root, in preparation.

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"Integrated Circuit Multiple Scaler With Buffered Memory," L. L. Lucas and J. W. Root, in preparation.

"A Dual Isotope Technique for the Measurement of Absolute Hot Yields in Nuclear Recoil Tritium Experiments," L. L. Lucas and J. W. Root, in preparation.

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"Atomic and Molecular Collision Dynamics in Very High Energy Chemical Systems," J. W. Root, Final Technical Report.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Chemical dynamics continues to emerge as one of the most active cross disciplinary areas in modern chemical research. The central problem in chemical dynamics involves studies of potential energy surfaces for atomic/molecular dynamical systems. This knowledge is central to the rigorous theoretical understanding of chemistry, as well as to the solution of many practical problems such as, for example, the prediction of thermodynamic and kinetic behavior for very high temperature fluids. To study a particular potential energy surface at points other than the lowest energy "saddle point" requires the investigation of high energy chemical systems.

There are serious gaps in our knowledge about chemical and physical phenomena in the energy range between 0.1 and 10 electron volts, corresponding to thermal energies in the range between 1000 and 100,000°K. New photochemical methods offer a powerful tool for chemical dynamics studies in the energy range from 0.1 to perhaps 5 electron volts. The utilization of these techniques is in its infancy.

This research was concerned with experiments in high energy photochemistry. The principal objectives of this work were (1) to provide definitive tests of modern theories about the molecular dynamics of simple activated chemical reactions, and (2) to provide new evidence about molecular properties and about chemical dynamics at energies above 0.1 electron volt.

The work included studies of the chemical phenomena of high energy alkyl free radicals and of the hot hydrogen abstraction reaction, together with the development of new methods for the calculation, correlation, and prediction of molecular sizes and chemical bond strengths.

Other work included photochemical studies of hot hydrogen abstraction, hydrogen replacement, and radical replacement reactions by energetic H, D, and CH T radicals.

The research areas exploited and the accomplishments are listed:

Steady State Theory of Hot Reactions.

Dr. Keizer and Dr. Root have developed a new statistical mechanical theory applicable for the description and interpretation of high energy chemical reactions. Two publications have resulted from this work.

Photochemical Threshold Studies.

This project, which involves phenomenological reaction threshold measurements, has been carried out in the laboratory by Dr. Tsao and Mr. Lan. To date, this program has been principally concerned with the elucidation of the special chemical characteristics of vibrationally hot methyl radicals. Two publications have resulted.

Behavior of Chemically Activated $^{14}CH_3CF_3$.

In a separate series of investigations, another aspect of the behavior of vibrationally hot species has been studied. In his Ph.D dissertation project, Dr. George W. Mutch investigated the collisional energy transfer behavior of hot $^{14}CH_3CF_3$, which was generated via the gas phase recombination of $^{14}CH_3$ plus CF_3 free radicals.

New and rather general results were obtained pertaining to the unimolecular behavior of fluorinated alkanes, and bimolecular energy transfer processes were characterized for $^{14}CH_3CF_3$ colliding with ethane and essentially all isomeric fluorinated ethanes. This $^{14}CH_3CF_3$ research, together with the previously described photochemical threshold studies, constitutes the first definitive investigation via radiotracer techniques into the chemical kinetic behavior of vibrationally excited species. These new experimental methods appear to be promising for a rather wide variety of applications.

Chemical Effects on Ion-Stopping Processes.

The Ph.D. dissertation research of Dr. Larry L. Lucas has involved basic studies of the chemical dependence of low velocity heavy ion stopping powers. It has been shown that these ion-stopping processes are relevant for a variety of practical applications, including ion implantation, ranges of hot heavy ions (including accelerated polyatomic species) in chemical materials, and energy transfer phenomena in ordinary radiolysis. Part of this work has been published.

AFOSR Program Manager: D. W. Elliott

COMPLETED PROJECT SUMMARY

1. TITLE: Ion Fragmentation of Organic Materials by Photoionization and Electron Impact

2. PRINCIPAL INVESTIGATOR: Dr. James W. Taylor
Department of Chemistry
University of Wisconsin
Madison, Wisconsin

3. INCLUSIVE DATES: 1 January 1969 - 31 December 1972

4. GRANT NO.: AFOSR-69-1725

5. COSTS AND FY SOURCE: $49,499 FY 69; $44,777 FY 70; $48,534 FY 71; $49,455 FY 72

6. SENIOR RESEARCH PERSONNEL: None

7. JUNIOR RESEARCH PERSONNEL:

F. Baudais	G. G. Jones
C. Garber	J. A. Kinsinger
A. Grange	D. L. Larsen
R. Hansen	G. R. Parr
R. Hilmer	W. L. Stebbings
B. M. Johnson	R. A. Valenzi

8. PUBLICATIONS:

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"Ion Fragmentation of Organic Materials by Photoionization and Electron Impact," J. W. Taylor, Final Technical Report.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The basic goals of the research were to gain a fundamental understanding of the important processes which govern the structure, lifetime, stabilization, and dissociation of ionic species in the gas phase. The gas phase work involved the use of the techniques of both electron and vacuum ultraviolet photon absorption, high and low resolution mass spectrometry, kinetic energy analysis of photoejected electrons (both PES and ESCA), fluorescence measurements, and charge exchange (both chemical ionization and ion-molecule) reactions. The use of the synchrotron-storage ring vacuum ultraviolet continuum light source provided a unique opportunity to gain control over, and thereby study and separate more efficiently, the pertinent processes which govern the absorption and ionization processes.

The basic aims of the research were directed toward a more fundamental understanding of both the photon and electron impact excitation and ionization processes which are important in mass spectrometry. Since initiation of the work, the scope was expanded to include other basic studies in the vacuum ultraviolet region of the spectrum which have a bearing on the question of what constitutes the nature of the bonding in a chemical compound and what are the consequences of the energy absorption process. Initially, the interest was in large organic compounds whose detailed fragmentation would provide insight into the important processes controlling the unimolecular decomposition reactions observed in a mass spectrometer. Later studies involved less complicated systems and included some of those atmospheric constituents which derive their importance from ecological considerations, such as oxygen and ozone. For some of these latter compounds, the instrumentation and techniques developed for the fundamental studies can also be used to provide absorption and ionization cross section measurements, photoelectron spectroscopic studies at variable wavelengths, and high energy photon excitation experiments which are difficult because of the limited number of broad continuum sources available in the laboratory. The reason some of these experiments could be accomplished was due to the availability at Wisconsin of the Physical Sciences Laboratory 240 MeV electron storage ring light source.

AFOSR Program Manager: Dr. A. J. Matuszko

COMPLETED PROJECT SUMMARY

1. TITLE: Oxidative Decomposition of Organic Materials and Reactivity of Organometallic Substances Related to Catalysis

2. PRINCIPAL INVESTIGATOR: Dr. Teddy G. Traylor
Department of Chemistry
University of California (San Diego)
La Jolla, California

3. INCLUSIVE DATES: 1 September 1968 - 28 February 1973

4. GRANT NO.: AF-AFOSR-69-1639

5. COSTS AND FY SOURCE: $43,587 FY 69; $37,913 FY 70; $35,421 FY 71
$38,945 FY 72

6. SENIOR RESEARCH PERSONNEL: Dr. N. Clinton, Dr. H. Kiefer, Dr. W. Hanstein, Dr. G. Koermer, Dr. J. Jerkunica, Dr. K. Munk

7. JUNIOR RESEARCH PERSONNEL: H. Berwin, R. Kenley, M. Hall, C. Lin, S. Hannon

8. PUBLICATIONS:

"Carbon-Metal Hyperconjugation. The Extraordinary Electron Donation by σ-Metalloalkyl Groups," W. Hanstein and T. G. Traylor, Tetrahedron Letters No. 45, 4451 (1967).

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"Free Radical Induced Decomposition of Peracetic Acid," R. A. Kenley and T. G. Traylor, in preparation for J. Amer. Chem. Soc.

"Termination Reactions in Aldehyde Autoxidations," R. A. Kenley and T. G. Traylor, in preparation for J. Amer. Chem. Soc.

"Oxidative Decomposition of Organic Materials and Reactivity of Organometallic Substances Related to Catalysis," T. G. Traylor, Final Technical Report.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

I. Processes related to autoxidation.

A study of the production and self-reactions of oxy and peroxy radicals has produced two advances. A safe, high efficiency, low temperature initiator, di-t-butyl hyponitrite $(CH_3)_3CONNOC(CH_3)_3$ has been produced. This compound also has sufficient vapor pressure to be useful as a gas-phase thermal initiator. The initiator has been used to study the cage behavior of t-butoxy radicals in solution. In addition, the gas-phase decomposition revealed a new kind of wall cage effect.

$$(tBuONNOtBu)_{adsorbed} \longrightarrow [tBuO\cdot N_2\cdot OtBu]_{adsorbed}$$

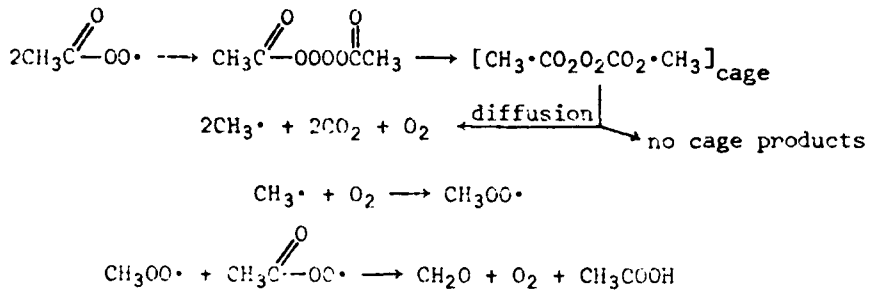
$$[tBuO\cdot N_2\cdot OtBu]_{adsorbed} \xrightarrow{\text{cage reaction}} [tBuOOtBu]_{adsorbed} \xrightarrow{\text{desorption}} (tBuOOtBu)$$

This wall effect has important implications in many gas-phase reactions.

Dr. Traylor and his co-workers used ^{18}O studies to determine the mechanisms for the interaction of acetylperoxy radicals. The radicals were produced either by autoxidation of acetaldehyde

$$CH_3CHO + RO\cdot \xrightarrow{O_2} ROH + CH_3\overset{\overset{O}{\parallel}}{C}-OO\cdot$$

The interaction mechanism is



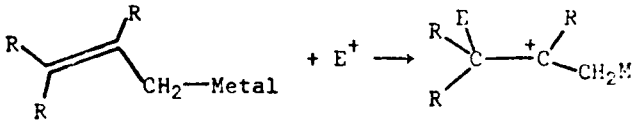
In addition to these reactions, there is a non-terminating reaction.

$$CH_3OO + CH_3CHO \longrightarrow CH_3CO + CH_3OOH$$

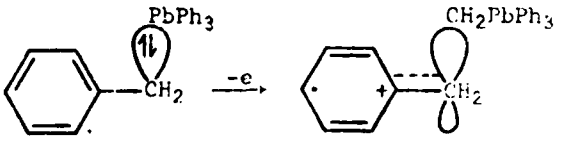
These mechanisms, added to those for hydrocarbon autoxidation, complete the mechanism for the oxidation of alkanes to carbon dioxide. While there are many steps involved, each of these steps is now understood.

II. Carbon-metal bonds and organic reactivity.

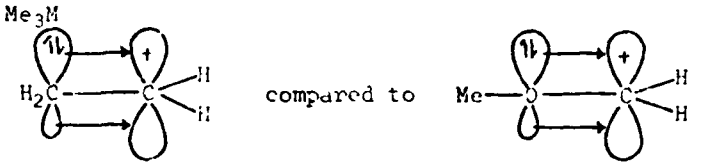
In a study of the reaction at remote positions in unsaturated organometallic compounds, for example



it was discovered that the carbon-metal bond is an extraordinarily powerful resonance stabilizing group, i.e., the ionization potential of benzene is lowered more than 1 eV by the CH_2PbPh_3 group.



Using photoelectron spectroscopy and charge-transfer spectra, it has been shown that metalloalkyl groups, e.g., Me_3MCH_2- can be better resonance stabilizing groups than MeO and some are comparable to $H_2\ddot{N}$-. This electron donation is operated by hyperconjugation (σ-π conjugation) and has been termed vertical stabilization to contrast it to neighboring group participation.



σ-π conjugation n-π conjugation

The importance of σ-π conjugation has been demonstrated for a wide variety of chemical reactions such as oxymercuration, deoxymercuration, aromatic electrophilic displacement of metals, allylmetal reactions, and electrophilic substitution on benzylmetal compounds.

The usefulness of the metallomethyl group in electrophilic aromatic substitution is clear from our observation that these groups R_3MCH_2- range in electron-donating ability from that of hydrogen to that of an amino group.

AFOSR Program Manager: Dr. A. J. Matuszko

COMPLETED PROJECT SUMMARY

1. TITLE: Gas Phase Spectrometric Analysis of Trace Elements

2. PRINCIPAL INVESTIGATOR: Dr. James D. Winefordner
Department of Chemistry
University of Florida
Gainesville, Florida

3. INCLUSIVE DATES: 1 November 1969 - 31 August 1973

4. GRANT NO.: AF-AFOSR-70-1880

5. COSTS AND FY SOURCE: $99,570 FY 70; $94,924 FY 71
$98,067 FY 72; $89,488 FY 73

6. SENIOR RESEARCH PERSONNEL:

Dr. P. Beckwith	Mr. L. Hart
Dr. P. Benetti	Dr. N. Omenetto
Dr. R. F. Browner	Mr. B. Patel
Dr. J. Fiorino	Dr. R. Reeves
Dr. T. H. Glenn	

7. JUNIOR RESEARCH PERSONNEL:

J. Ahlstrom	M. Fraser
M. Black	M. Glenn
T. Booker	L. Hart
C. Chen	D. Knapp
T. Chester	C. Molnar
F. S. Chuang	G. Nitis
R. Cooney	F. Plankey
R. Elser	J. Sarbeck
R. Fisher	B. Smith
J. Fitzgerald	S. Weeks
W. Fowler	

PUBLICATIONS:

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"A Combination Flame Atomic Fluorescence-Atomic Emission DC Spectrometer for Analysis of Trace Wear Metals in Jet Engine Oils," R. L. Miller, L. M. Fraser, and J. D. Winefordner, Appl. Spectrosc., 25, 477 (1971).

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9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The AFOSR Program on Trace Spectrometric Flame Analysis and Gas Chromatographic Detectors Related to Jet Engine Oil Analysis and Gas Detection at the University of Florida consists of fundamental, instrumental, and applied studies of atomic and molecular emission, atomic absorption, and atomic and molecular fluorescence of gases and of development of gas chromatographic detectors. By means of such studies, new and improved selective, sensitive methods of trace analysis of elements and molecules in the gas state or convertible to the gas state are being developed. Special emphasis has been given to rapid simultaneous and rapid sequential multielement analysis of several elements or species.

Fundamental Studies. A variety of physical and spectroscopic parameters either characteristic of the flame only, such as the flame temperature, T, or the flame and the atomic species of concern, such as the free atom fractions, β (degree of atomization), the quantum yields, Y, and the damping constants, a (approximately the ratio of collisional to Doppler broadening) of a number of atoms in a variety of flames have been measured and compared with previously measured and/or calculated values. These parameters are extremely important in terms of optimization of experimental conditions and atomic emission, atomic absorption, and atomic fluorescence flame spectrometry. In fact, in all three of these atomic methods, the measured signals will be directly proportional to β which depends critically upon T. In atomic fluorescence flame spectrometry, the measured signal will be additionally directly proportional to Y which also depends on T, but less critically than β. In atomic emission flame spectrometry, the measured signal will always be critically dependent upon T. The shapes of the analytical curves (measured signal vs. concentration of analyte) will in all three methods depend upon the value of a. Experimental verification of theoretical predictions was performed. In atomic fluorescence flame spectrometry, the shape of the analytical curve also depends upon the geometric arrangement of exciting source, flame, and measurement system.

Because of the importance of scatter of exciting radiation in atomic absorption and atomic fluorescence flame spectrometry, a critical study of scattering indicated that the scatter of radiation from particles (droplets) in flames is not Rayleigh scattering as has been assumed previously and can be relatively reduced compared to the atomic fluorescence signals with crossed excitation and emission polarizers (continuum excitation source).

Several new methods of flame temperature measurement have been developed. By means of an atomic absorption method in which the ratio of the fraction of radiation absorbed, α, for atoms with two spectral lines having different lower energy states and similar wavelengths, e.g., In-410.18 nm and 451.13 nm, temperatures for $Ar/O_2/H_2$, air/C_2H_2, and N_2O/C_2H_2 flames were determined with errors less than 20°K. A color temperature method based on atomic fluorescence spectrometry allowed similar results; in this latter method, two atomic fluorescence lines of an element, like Tl with two lines having the same upper level (377.6 and 535.0 nm) are excited with a continuum source of variable color temperature, and by a simple calculation, the flame temperature is determined.

Other fundamental studies of flames and species in flames included the study of the temperature effect on the collisional half widths of the In-410.2 nm and 451.1 nm lines, the classification of laser excited atomic fluorescence transitions, and the decay of atomic population above a graphite filament upon thermal atomization of samples placed on the filament. In addition, information theory has been shown to be quite useful in selecting a method for a given analysis. And signal-to-noise ratios have been stressed as the parameter to measure when optimizing a given procedure.

The influence of intense radiation (lasers) upon both the atomic absorption and atomic fluorescence irradiances has been discussed, and theoretical expressions have been given to determine the variation of absorption and fluorescence irradiances with source irradiance and with quantum yield of fluorescence. It is shown that at high source irradiances, the absorption signal becomes small and the fluorescence signal becomes independent of source irradiance and analyte atom quantum yield. In addition, the analytical (growth) curves become linear over a much greater concentration range if the source irradiance is large, i.e., the atomic levels approach saturation (equal population of lower and upper levels assuming equal statistical weights).

An extensive study of the effect of microwave power and lamp temperature of electrodeless discharge lamps operated with a thermostated "A" antenna and with a thermostated and an unthermostated 3/4-wave cavity has been performed. It is shown that the lamp temperature is by far the most critical factor in operating electrodeless discharge lamps (EDLs) for atomic absorption and atomic fluorescence spectrometry. It is also shown that the radiation emitted by EDLs is not self-absorbed or self-reversed, and that the EDLs seldom exhibit only a skin effect. Helium fill gas (5 Torr) results in greatest line intensities, but since He diffuses through the lamp walls, Ar at 0.5 Torr is optimal for operation of EDLs.

Instrumental and Methodological Studies. Two selective gas chromatographic detectors were developed. One of them was based on the conversion of a halogenated sample into fragments consisting of NX (X is a halogen) and other species and passing the HX past a hot In surface to produce InX which resulted in characteristic emission in a flame. The other detector was based upon passage of the chromatographic effluent through an Rf plasma and measuring the emission of characteristic species (radicals).

Because of the advantages of non-flame cells in atomic absorption and atomic fluorescence as compared to flame atomizers, e.g., low background, long atomic residence times, good atomization, and low concentration of quenchers, much research has been done on the development of both the heated wire loop and graphite filament atomizers. These atomizers have been found to atomize all volatile elements, as Cd, Zn, Hg, In, Ga, Tl, Se, Te, As, Bi, Sb, etc., as well as less volatile elements as Fe, Cr, Mn, Ni, etc. The decay of atomic population above these atomizers as well as the gas temperature above these atomizers has been measured. Also, atomizer temperature, inert gas flow rate past the atomizers, and compound type placed on the atomizers have been thoroughly studied. In addition to these two atomizers, a continuous flow, non-flame atomizer has also been evaluated for atomic fluorescence spectrometry.

Most of the studies involving instrumentation and methodology during the past four years have involved the development of single and multi-element electrodeless discharge lamps (EDLs) and the optimal coupling of microwave energy into these lamps. EDLs have been produced for about 70 elements. Other sources studied include the Eimac 150 W xenon lamp, the Osram 150-900 W xenon lamp, hollow cathode discharge lamps, and a tunable dye laser pumped with a pulsed Na laser. The latter source is nearly ideal for atomic fluorescence spectrometry because it is intense (10-50 kW peak power), has a low duty cycle (about 10^{-8}, i.e., it is "on" for one part in 10^{8} parts) which results in improved detection limits as long as a gated detector is used, is simple to align and operate (collimated beam), is selective in excitation of non-resonance lines to avoid scattering problems, and results in near saturation of atomic energy levels; also the source intensity and atomic quantum yields have little effect on the measured fluorescence signals and longer linear analytical curves result. The laser has been used to excite the atomic fluorescence (in flames) of most of the transition metals, the rare earths, the soft metals, and the alkaline earth elements. By means of a tunable dye laser, a large variety of non-resonance Stokes and Anti-Stokes lines are observed for atoms in flames.

Several studies involving the use of a spectral continuum excitation source in atomic absorption and atomic fluorescence spectrometry have been performed. These studies utilize a single source for excitation of virtually all elements atomized in a flame. One method utilized an oscillating Fabry-Perot interferometer coupled to a grating monochromator to modulate a small spectral interval about the absorption line. In the other method, double modulation is used to eliminate flame emission and molecular absorption-scattering interference-double modulation implies modulation of the source at one frequency and the wavelength of the monochromator at another frequency. In both systems, the detector signal is detected with a phase-sensitive detector.

A spectrometric system in which the exit slit-photodetector assembly has been replaced with an image vidicon has been shown to have considerable use for multi-element atomic spectrometry.

Other studies performed include the use of an elliptical mirror arrangement to increase the source irradiance on a flame in atomic fluorescence spectrometry, the use of a continuous flow system for microsamples measured by atomic emission and atomic fluorescence spectrometry, the use of a simple, inexpensive, flat steel optical bench for spectroscopic studies, a monochromatorless system for atomic fluorescence spectrometry, and a power divider system to operate two thermostated electrodeless discharge lamps simultaneously from the same microwave power supply.

Applications. All applications have included the use of flame and non-flame atomic absorption and atomic fluorescence spectrometry to determine trace elements in blood serum samples and in jet engine and reciprocating engine oil samples.

Reviews. During the past four years, review articles have been written on a critical comparison of atomic emission, atomic absorption, and atomic fluorescence flame spectrometry, on atomic fluorescence spectrometry, on non-flame cells in atomic fluorescence spectrometry, on flame spectrometry, on atomic absorption spectrometry, and on the use of information theory in analytical chemistry.

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